PART I. THE THERMODYNAMIC FUNCTIONS FOR THE FORMATION OF SOME MOLECULAR COMPOUNDS IN SOLUTION

PART II. THE IONIZATION CONSTANTS OF SOME PARA-SUBSTITUTED p'-DIMETHYLAMINOAZOBENZENES

By

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I. INTRODUCTION

A large number of compounds are known as addition compounds. The term "addition compound" refers to a method of preparing these substances, there being only one product in an addition reaction. An addition compound may be one of three types:

A. Nothing but simple valences exist. An example is ethylene bromide which is the only product formed when hydrogen bromide is added to ethylene.

B. The valences that exist represent an extension of the simple valence theory. Ammonium chloride is such a compound because here nitrogen has a valence of four, giving the ion its charge. Oxonium salts are included in this type.

C. A third type of addition compound is represented by molecular compounds, which may be divided into three groups: (1) complexes which are held together by means of a hydrogen bond; (2) quinhydrones, which are highly colored complexes of quinone or a substance with a similar structure with an aromatic substance like aniline, phenol or hydroquinone (the hydrogen bond is important here also); (3) addition compounds of polynitro compounds, or in a few cases, compounds similar to polynitro compounds, with aromatic amines, hydrocarbons, and phenols.

The term "molecular compound" will be used to refer only to substances formed from polynitro compounds or similar compounds. The other types of molecular compounds are not discussed in this paper.

Use of the term "molecular compound" implies that the interaction leads to compound formation. Since the question of whether or not there is compound formation is part of the principal problem of this paper, this term is used only as a convenient one, and it is not to be inferred that the answer to this problem is assumed.

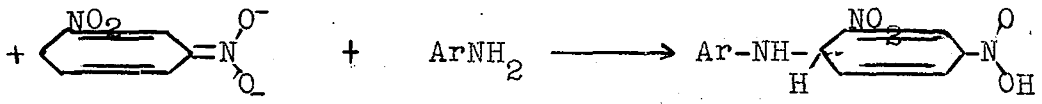
There is no general agreement concerning the nature of the attraction force existing between the components of a molecular compound. (1) It is the purpose of this paper (1) to discuss the theories of the nature of this interaction and the evidence for these theories given in the literature and (2) to present experimental evidence intended to clarify certain aspects of the problem.

II. SUMMARY OF PREVIOUS RESULTS

A. Theories explaining the interaction between the components of a molecular compound. 1. *The covalent bond theory*. That there is a definite covalent bond involved in molecular compound formation is suggested by several workers. Three different kinds of covalent bonds are postulated:

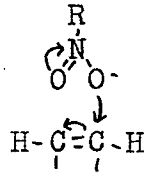
a. Bennett and Willis (2) suggest that one ethylenic double bond in the unsaturated hydrocarbon component is polarized and that the negative carbon atom thus produced is linked to the nitrogen atom of a nitro group.

b. Sudborough (3) postulated a carbon-carbon covalent bond. Later he abandoned this idea for the residual valence theory. (4) Buehler, Hisey, and Wood (5) also suggest this carbon-carbon covalent bond. Bennett (6) abandoned his earlier view of the carbon-nitrogen bond, and accepted the idea of a carbon-carbon bond or in the case of amines, a carbon-nitrogen bond, as is shown for amines:



c. A reaction of the ethylenic bond with the oxygen atoms of the nitro group was postulated by Hammick and Sixsmith. (7)

Structure I leads to Structure II.



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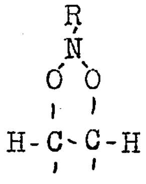


II

This results from the same ethylenic polarization as presented in (a.) and (b.) According to the theory, the nitro group does not react in this manner unless there is something in R which attracts electrons. Hammick later abandoned this idea for the polarization theory.

2. <u>The residual valence theory</u>. Sudborough (4) elaborates on the theory of Pfeiffer (8) who explains some of the interactions of phenols and amines with quinones and aromatic hydrocarbons. Sudborough suggests: $C_6H_3(NO_2)_3$ ...... $C_{10}H_8$ for the interaction between s-trinitrobenzene and naphthalene. The residual valence of the whole aromatic molecule interacts with the residual valence of the nitro group. This idea was also supported by Kenner and Parkin. (9) Later it was pointed out by Shinomiya (10) that there is another type of residual valence typified by the interaction between naphthylamine and picric acid: $C_{10}H_7NH_2$ .....$HOC_6H_2(NO_2)_3$. According to Shinomiya this latter interaction does not show a large color change, as contrasted with the noticeable coloration

produced by the interaction between s-trinitrobenzene and naphthalene.

3. The coordination theory. Lowry (11) suggests there is a coordination between the components which form molecular compounds. It may be that a hydrogen atom in the hydrocarbon molecule attracts a "lone pair" of electrons on a nitrogen, oxygen, or halogen atom. This view is not clarified further by him.

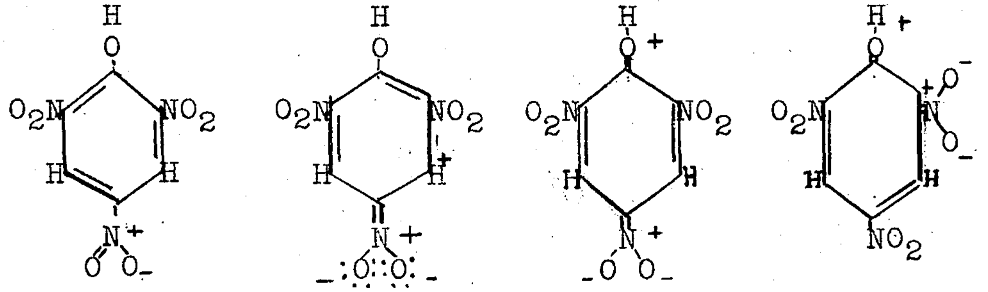
4. The polarization theory. The idea is advanced by several workers that the phenomena observed in molecular compounds may be explained by a polarization interaction between the nitro group and the hydrocarbon molecule. There are five different views on polarization.

a. The aromatic hydrocarbons which form molecular compounds are unsaturated and are polarizable. The permanent dipole of the nitro group induces a dipole in the hydrocarbon molecule. The two molecules together are called a dipole aggregate. This idea is advanced by Briegleb and his coworkers. (12-17)

b. Gibson and Loeffler (18) say that the polarization is actually an incipient oxidation-reduction reaction. For example, it is polarization that necessarily precedes the reduction of nitrobenzene. This reduction does not occur when an amine such as aniline is mixed with nitrobenzene. There is, however, a polarization interaction, since a color is produced.

c. Hammick (19) abandoned his earlier idea of covalent bond formation and accepted the polarization theory. He suggests the interaction is not very different from that between molecules of a liquid, except that there is some orientation in molecular compound complexes. The polarization aggregate that produces color is not, however, the dipole aggregate of Briegleb; with the polarization aggregate there actually is an incipient chemical reaction.

d. Pauling, (20) in accepting the polarization theory, ascribes the color so commonly associated with molecular compounds to the stabilization of certain resonance contributions of nitro molecules by a hydrocarbon molecule. Some of the resonance contributions to picric acid are:

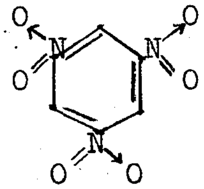
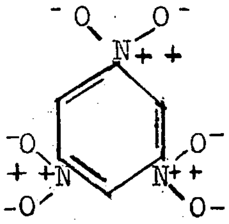
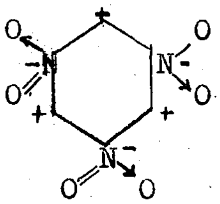


He states that coulombic energy is important in ultraviolet and visible spectra, and that structures having a charge separation, as do those shown, give the compound color. Since aromatic hydrocarbons are easily polarized, and the hydrocarbon molecule can come within

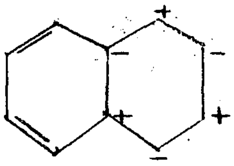
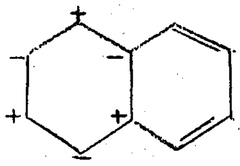
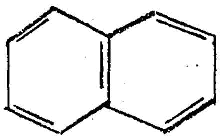
3.5 Å. of the nitro molecule, the effective dielectric constant in the region around the nitro molecule is greatly increased. The coulombic energy of separation of the charge is therefore proportionately decreased; structures with separation of charge are stabilized, and color is enhanced.

No attempt is made to explain other phenomena of molecular compounds, as electrical properties and equilibrium constants in solution.

e. Recently there has been an interesting modification of the polarization theory advanced by Sahney and coworkers. (21) They say s-trinitrobenzene has these contributing structures:

It interacts with naphthalene, which can have the contributing structures:

They show the first two to be the actual structures. The molecular interaction is a polarization of the hydrocarbon molecule by the nitro molecule. In the molecular compound that is formed the second structure which is the most highly polarized of those shown for s-trinitrobenzene becomes most important, while the third structure of naphthalene which is least polarized becomes most important.

5. The ionization theory. The reaction

$$A + B \longrightarrow (AB) \longrightarrow (A)^{+}(B)^{-}$$

is postulated by Weiss. (22) In this equation A is a donor molecule such as an aromatic hydrocarbon or amine, and B is an acceptor molecule such as an aromatic nitro compound. In the reaction there is a transition complex, (AB), which probably forms from A and B through dipole and dispersion interactions. When this complex forms, there is a bond with a large amount of ionic character formed by means of an electron transfer. The polar molecule thus formed dissociates into ions. The amount of this dissociation depends upon the nature of A and of B and upon the nature of the solvent. Ionizing solvents favor this dissociation. Probably the equilibrium constant for the formation of the transition complex is always large.

B. Discussion of the evidence for the different theories.

After one has postulated the nature of the interaction between the components which make up the molecular compound in solution, it is desirable to find one or more physical or chemical properties which prove conclusively the postulated interaction. Most properties, however, do not meet this rigid requirement: all but a very few can be consistent with two or more proposed interactions. It is therefore necessary to examine carefully these properties. In this section some of these properties and their significance in relation to the proposed interactions are discussed.

1. The rate of formation of molecular compounds. If the rate of formation of a molecular compound were slow, this fact would be evidence for the existence of a covalent linkage. The only case of a detectable rate of formation of a molecular compound is reported by Hammick and Sixsmith (7) who say that the complex between indene and methyl-4,6,4',6'-tetranitrodiphenate may be formed and deformed at a finite rate in carbon tetrachloride. They determine the rate by titrating with bromine; the amount of bromine used by the solution decreases with time, indicating the ethylenic linkage is inactivated in the complex. They calculate the equilibrium constant from rate data (both formation and deformation) and from experimental data; these values agree within experimental error. This data would be convincing if valid. Hammick (19) later admits there must have been an error, although the experiment was repeated with the same results. In the present paper two reasons are given for questioning these results.

a. No finite rate of formation is reported in the literature for any other molecular compound. Mixing toluene and tetranitromethane at -96° produces color immediately;

the rate of formation would probably be detectable at this low temperature if a covalent bond were formed.
b. Dr. M. T. Rogers (23) who attempted to repeat the early work of Hammick and Sixsmith on the indene complex by noting the color produced found there is no change in total color with time.

If it is true, as Hammick states in the earlier work, that the only requirement for covalent bond formation is that there be, in at least some cases, a measurable rate of formation, then it must be concluded there is no covalent bond formation. Whether or not this is the only requirement is no longer of interest, since other properties discussed here show conclusively there is no covalent bond formed.

Since there is no observable rate of formation noted, the nature of the interaction eventually chosen must be such that a rapid rate is possible. It is certainly true that such a rate is consistent with all the polarization and the ionic theories; it may not hold for the residual valence theories.

Weiss (22) discusses theoretically the rate of formation of an ionic molecular compound, and he shows the rate will be very rapid except for the case in which the equilibrium constant for the formation of the transition complex from the initial state is small; he thinks that this may be true in the case of the indene complex mentioned above.

2. Measurements made on the solid state. The primary consideration of this paper is the nature of the molecular compound in solution, but it is necessary to discuss certain properties of the solid state, because they aid in disclosing the nature of the corresponding solutions.

It is not necessarily true that a molecular compound can be isolated as a solid if it forms in solution. It may be, as is probably the case with tetranitromethane compounds with aromatic hydrocarbons, that the amount of compound formed is never large enough to exceed the solubility of that compound in any solvent used. This would be true even with mixtures of the pure components in any proportion. There are steric and other factors which aid the formation of a crystalline lattice in some cases. Where these favorable factors are absent, the tendency to form a crystalline lattice may also be absent, even though the compound is relatively stable. There may also be instances in which crystals are stabilized principally by these favorable factors. These things confuse the "order of stability" when determined in the solid state.

Hammick and coworkers (24, 25) report phase diagrams for several systems in which solid molecular compounds might be expected to form. Most of the data reported is for interactions between

4,6,4',6'-tetranitrodiphenate and several aromatic hydrocarbons. The diagrams indicate that in several cases compounds do form, but that in some others they do not. All mixtures in the liquid state give color. This further shows that the conditions favorable for compound formation are not the same as those for solid formation, if it can be assumed color indicates compound formation.

The values of the melting points are discussed in the literature. Kronberger and Weiss (26) point out that metal halides which break up into polar molecules, not ions, melt at low temperatures. (27) They suggest that much the same situation exists with molecular compounds which according to their theory, also break up into polar molecules upon melting. The polar molecules subsequently break up into ions to a slight extent.

According to Powell and Huse (28) the low melting points of molecular compounds--usually not far different from those of the components--indicate the binding forces in molecular compounds are no stronger than the binding forces of the original molecular crystals. Much higher melting points would be expected, they say, if ionic crystals broke up into ions upon melting. They ignore the above theory of Kronberger and Weiss. It is not easy to predict what the melting point would be for the other types of interaction suggested. If a covalent bond were formed the melting point would be determined by the magnitude of the dissociation and recombination effects.

The crystal structure of molecular compounds has been the subject of some debate. There have been reported intermolecular distances of the order of 3.2 Å, as with p-iodoaniline-s-trinitrobenzene reported by Powell and coworkers. (29) Acenaphthene-2,6-dinitroxylene, which Hertel and Kleu report, (30) has the sodium chloride type face-centered cubic structure.

Powell, among others, says that an intermolecular distance of 3.2 Å is too great for covalent bond formation. Powell and Huse (28) discuss the possibility of an ionic bond and reject it not only on the basis of the melting point already cited, but also on the basis of crystal structure, diffuse X-ray spectra, and the falling off of intensity of X-ray spectra with increasing Bragg angle θ. In the p-iodoaniline-s-trinitrobenzene compound mentioned above and in the picryl halide-hexamethylbenzene compounds described in the later paper the molecular crystal is pictured as one of alternate layers of hydrocarbon and nitro compound; they say this suggests something other than the ionic bond. Weiss points out in referring to the work of Hund (27) that large polarizable ions would tend to form layer lattices. Intense diffuse X-ray spectra are found in crystals where there are planes held by weak forces. Such diffuse spectra are found in the picryl halide molecular compounds examined. The intensity of all X-ray reflections falls off as the Bragg angle, θ, increases in such weak crystals, as is found with the molecular compounds examined.

The only objection of Powell and Huse that remains is the structural objection; according to Kronberger and Weiss (26) the presence of the electronegative iodine atom on the donor molecules makes these non-typical cases. Kronberger and Weiss do not discuss the instances in which the iodine atom is not present. Later Powell concluded (31) that some of the inter-atomic distances in these molecules are too small for the attracting forces to be van der Waals forces. The objection that X-ray analysis shows there are weak bonds does not seem to be applicable: there is ample evidence that the interaction energy in dilute solution is small, suggesting that the same is true in the crystal. The weak ionic bond postulated is discussed more fully in the section on heats of reaction.

More recent work by Saunder (32) shows that there are weak bonds in the molecular crystal of 4,4'-dinitrodiphenyl and 4-hydroxybiphenyl. Essentially the same results as those obtained for the other crystals mentioned are given.

The intermolecular distances are considered by Weiss (22) in connection with the ionic theory. Inorganic ions are spherical, while ions of molecular compounds are flat, parallel plates that are much larger than inorganic ions and are, therefore, more polarizable. The interionic distances in molecular compounds are of the same order of magnitude as in some inorganic crystals of univalent ions--such as 3.15 Å for potassium chloride. The existence of the sodium chloride type lattice, for acenaphthene-2,6-dinitro-m-xylene is further evidence for the ionic structure.

The so-called "radius of action" of the carbon atom is about 1.6 Å. The distance between the parallel plates would have to be about twice this value. Weiss points out that the distances actually are about 3.2 Å. The radius of the positive ion would be a little less than 1.6 Å. and that of the negative ion a little more.

It is apparent that the best Weiss can do in discussing the crystal structure of molecular compounds is to show that the evidence in the literature is not inconsistent with the ionic theory. This attempt is sometimes labored, but it seems that there is as yet insufficient evidence from crystal data to prove or disprove the ionic theory.

3. The nature of the "donor" and the "acceptor" molecules. There is general agreement that for an interaction of the kind being discussed to take place one of the molecules must tend to give electrons and the other must tend to accept electrons. For the sake of brevity the terms "donor" and "acceptor" molecules are used; it is not intended that these terms should decide the nature of the interaction. Some molecules which tend to give electrons are aromatic hydrocarbons, conjugated unsaturated aliphatic compounds, and derivatives of aromatic hydrocarbons, such as amines in which electrons are donated to the ring by the amino group; those which tend to receive electrons are aromatic nitro compounds and aromatic compounds which have substituents similar to the nitro group.

a. The donor molecule. (1) Aromatic. The donor molecule must have a low ionization potential. These molecules all have loosely bound π electrons and in some respects they act like metals. London (33) points this out for conjugated, unsaturated aliphatic compounds. It would be expected that the lower the ionization potential, the greater the energy of interaction. The polarizability of the donor molecule is undoubtedly a parallel function; Briegleb and coworkers (13,14) show the energy of interaction increases as polarizability increases. Polarizability and energy of interaction increase with, for example, increasing number of fused aromatic nuclei in proceeding from benzene to naphthalene to anthracene to chrysene.

The number of nuclei in one donor molecule that can interact in solution differs in the various interaction theories. Some workers who assume a residual valence theory or a covalence theory, such as Sudborough (4) and Bennett and Wain (6), believe that two separated benzene nuclei, as in anthracene and diphenyl, can interact independently of each other. However, as shown in the section on equilibrium measurements, many workers show that equilibrium constants are obtained for the reaction in solution with the assumption there is a 1:1 reaction. In the polarization and ionic theories it would seem more reasonable to expect a 1:1 reaction in most cases since the electron cloud of the whole planar hydrocarbon molecule probably can be acted upon by the acceptor molecule. There may be exceptions. Weiss (22), as well as Kuhn and Winterstein (34), suggests that there may be two separate regions of influence in the same molecule. This would mean that there is a doubly charged ion which may be either positive or negative, leading to 2:1 compound formation. It must be remembered that solid state evidence given is particularly unreliable in such a question. Spatial arrangements are likely to be more important than a "region of influence".

Bamberger and Dimroth (35) obtain much the same result for condensed aromatic hydrocarbons as Briegleb; they measure the solubilities of the molecular compound of picric acid to determine the equilibrium constant.

It would be expected that if substituents of the benzene nucleus cause an increase in the electron density of the ring, there would be more interaction. Davies and Hammick (36) use the number of interactions, that is, a number proportional to the equilibrium constant, instead of the energy of interaction, to determine the relative stability of methylated benzenes. They find that in proceeding stepwise from benzene to hexamethylbenzene that the relative stability increases a thousand-fold. Their method is open to question, as is discussed in the section on equilibrium measurements, but their general conclusion undoubtedly is valid, since it is well established that methyl groups donate electrons to the ring.

Shinomiya (37, 38, 39) determines the effect of compound stability in the solid state--measured by melting points and examination of phase diagrams--of fourteen substituents on the aromatic hydrocarbon; half are more active, and half are less active than the parent hydrocarbon. The order of activity is about as expected; the groups which are least active are electron accepting groups, such as the nitro and cyano groups.

Briegleb (12) shows that if a side chain on benzene is conjugated with the ring, e. g. styrene, phenyl butadiene, and diphenyl butadiene, there is much greater interaction than with benzene itself; increased conjugation in the side chain increases the amount of interaction.

The nitro group, which accepts electrons from the ring, will, however, permit compound formation. Moore, Shepherd, and Goodall (40) report a pale yellow solid compound of picric acid with a nitronaphthalene; other similar compounds are nitrobenzene-dinitrobenzene (1:1) and nitrobenzene-s-trinitrobenzene (2:1). These are all weak interactions, and probably the nitro group in the donor molecule affects the interaction in no other way than by hindering it.

From their work Moore, Shepherd, and Goodall, among others, make the same conclusion concerning the general nature of the donor molecule. The equilibrium concentration of picric acid is determined in the presence of various substituted benzenes. Their methods are discussed in the section on equilibrium measurements.

Aromatic amines constitute the strongest kind of donor molecule in molecular compounds, and they react not only with aromatic and aliphatic nitro compounds, but also with nitroso compounds, quinones (41) and liquid sulfur dioxide. (42) Gibson and Loeffler (18) show that an aliphatic amine like α-phenylethylamine, even though it is a stronger base than aniline, will not react. Amines must be aromatic or, perhaps, conjugated with the ring in order to react. The color observed indicates that methyl groups on the amino nitrogen increase the stability of the molecular compound. These authors take the viewpoint that the amino group focuses the electrons of the ring and the group itself so that the inductomeric polarization is aided. The difference between hydrocarbons and amines is then only one of degree.

Weiss (22) thinks that groups like the amino group increase the strength of the electron cloud; this is not a focusing effect. It is difficult to see how the amino group could be said to focus the electrons in the solid state, where the donor and acceptor molecules probably lie in alternate parallel planes. This does not mean that the amino group could not focus electrons in solution.

(2) Aliphatic. If a molecule must be surrounded with an unusually dense electron cloud to be a donor

molecule in a molecular compound, it would be expected that some conjugated aliphatic chains would take part in such a reaction. Briegleb (12) points out that every nitro group must be able to interact with all the polarizable bonds; this means not only that the two interacting molecules cannot lie in the same plane, but it also means long chains cannot interact well. Conjugated chains are not as polarizable as ring systems of equal length; and so a short chain would be expected to cause weak interaction, if any. This Briegleb shows to be true for 1,3-butadiene, the energy of interaction, his criterion for stability, between this compound and s-trinitrobenzene being much less than 0.6 kilocalorie. Benzene, which has by far the smallest value of the aromatic hydrocarbons, has an interaction energy of 0.6 kilocalorie with s-trinitrobenzene.

b. The acceptor molecule. (1) Aromatic. Such molecules have a high electron affinity. One of the resonance contributions of an aromatic nitro molecule is a structure in which both oxygen atoms of the nitro group carry a single negative charge; in this the nitro group accepts electrons from the ring. The nitro group will aid in this same process by the inductive effect. Ordinarily another part of the same molecule is the source of these electrons. The ionic theory says that in molecular compounds there is an outside source of electrons by which the molecule acquires a charge.

Substituents other than the nitro group are known to have properties similar to those of the nitro group. It would be expected that substances other than nitro compounds could act as acceptor molecules in molecular compounds. Bennett and Wain (6) have actually observed the color effect typical of molecular compounds in solution for 1,3,5-tricyanobenzene and for the acid chloride of trimesic acid which is also symmetrical. The cyano compound gives a color with each of two amines, and the acid chloride with five hydrocarbons and one amine.

The number of groups on the aromatic nucleus of an acceptor molecule affects the strength of the molecular compound interaction. No studies are reported in this connection for groups other than the nitro group. Briegleb and others (13,17,43,44) show that with a given hydrocarbon the energy of interaction increases with the number of nitro groups. With acenaphthene or naphthalene, for example, the energy of interaction decreases from s-trinitrobenzene to m-dinitrobenzene.

Gibson and Loeffler (18) are unable to find evidence in the literature of the existence of any mononitro solid molecular compound. There may be some contrary evidence. (45,46) Whether or not a few mononitro solid molecular compounds exist does not alter the general conclusion that stability of the complex formed increases with the number of nitro groups. As is pointed out elsewhere, solid formation is no absolute criterion of stability, but the compound must have at least a certain amount of stability if its concentration is sufficient to make possible solid formation. It is very likely that all, or almost all, of the mononitro compounds are too unstable to be present in sufficient concentration for the solid to form.

It would be expected from the ionic theory that substituents other than the nitro group in the nitro molecule would produce an effect similar to the effect of the nitro group. There are no substituents which can accept electrons as well as the nitro group, but there are some which can receive electrons from the ring in positions ortho and para to a nitro group, making it easier for the nitro group to receive a charge.

Picric acid affords the best known example of a nitro compound in which another substituent plays a role in molecular compound formation. The comparative stability of picric acid-aromatic hydrocarbon compounds is well known. The reaction is not an acid-base reaction, but one in which the hydroxy group tends to receive electrons from the positions which are ortho and para to the three nitro groups. It is possible for picric acid to act as an acid in reactions involving strong bases, but this reaction does not represent molecular compound formation. However, the hydroxy group does not aid this process much, since it does not accept electrons well.

Buehler and others (47,48) show that the presence of the hydroxy group in the ortho or para position stabilizes the molecular compound only slightly in comparison with the nitro compound which has no substituent. They also report the effect of several other substituents on the stability of the molecular compound formed from the nitro compound. The substituent in the most stable compound is given first: Cl, Br, OH, H, CH_3, NH_2. The nature of these groups is well known and the order of stability is what would be expected if the stability depends upon the ease with which the nitro group can accept an electron.

(2) Aliphatic. It is not necessary that the nitro compound be aromatic. Tetranitromethane (12,49) is well known to give deep color with many donor molecules, although no solid compounds have been isolated. The colored solutions have been studied at

length, and there is no doubt that the interaction is that which is characteristic of molecular compound formation. This is not restricted to tetranitromethane; Will (50) reports that hexanitroethane imparts a yellow color to benzene or to toluene, as well as forming a red compound with naphthalene.

The relation between aromatic and aliphatic nitro compounds in molecular compound formation is discussed by Briegleb (12) who concludes that since the stability of tetranitromethane complexes is smaller than polynitro aromatic compound complexes, the difference is due to the freedom of the nitro groups. The freer they are with respect to each other, the greater the interaction with donor molecules. He does not prove mathematically that the interaction energy (which he calculates theoretically, as well as obtaining it from experiment) decreases as the nitro groups become closer to each other. If the energy of interaction is to be explained by the ionic theory, it is also possible to explain the difference between aliphatic and aromatic nitro compounds. It is much easier for nitro groups to donate electrons to the ring than to donate electrons to the carbon atom in tetranitromethane. In both cases the received electron would oscillate between several nitro groups; this is much easier where the nitrogen-oxygen bond is conjugated with the ring.

(4) The color of molecular compounds. Molecular compounds are known to have a deep color in solution, and this is usually, although not always, carried over to the solid state. The color produced is always deeper than that of the components. Since the absorption of light is undoubtedly closely connected with the interaction between donor molecules and acceptor molecules, a close examination of color phenomena should be important in the study of these compounds. The observed color, reported in many papers and in this work, is usually not given adequate treatment. Hunter and coworkers (51) dismiss the cause of the color with the remark, "Colour is produced by deformation which throws absorption into the visible region." The actual nature of this "deformation" (of the electron cloud) is of interest, and it has been discussed at length in a few papers.

No absorption peaks characteristic of the molecular compound have been observed. This probably indicates the color observed is merely a shift of the absorption of at least one of the components towards the red. These solutions vary from a faint yellow to a deep red. There seems to be no correlation between the absorption shift of either component and the stability of the molecular compound formed (measured by equilibrium constants and heats of interaction).

According to Weiss, (22) ions are formed having an odd number of electrons. This means there is an unoccupied energy level, and only a small excitation energy is required for absorption. Mullikan (52) says that resonance structures, such as these, which have a separation of charge, have strong visible absorption. Weiss (53) also makes a comparison of molecular compounds of aromatic hydrocarbons with s-trinitrobenzene and the molecular compounds of some fully conjugated ketones with s-trinitrobenzene. These ketones show deep color when protonated due to large loss of electrons on the part of the ketone. This loss of electrons is ion formation. Since these ketones also give a deep color with the formation of molecular compounds, this is certainly consistent with, but not proof of, the ionic theory.

Weiss describes the interaction in systems in which there are separated spheres of influence. Here 1:2 compounds may form. First one region of influence reacts to give a 1:1 compound, and this compound acts as a donor or acceptor molecule and reacts to form a doubly charged ion. Such a doubly charged ion has an even number of electrons, and it is not as deeply colored as the free-radical-like ion of the 1:1 compound, which has an odd number of electrons.

Briegleb (12) associates the loosely bound electrons, which in his theory, are polarized by the nitro compound, with the visible absorption noted. Hammick and Yule (19) point out that there are known dipole interactions, such as those in which different nitro compounds are mixed with each other, which do not produce color as would be expected according to the theory of Briegleb. It is pointed out by Hammick and coworkers (54) that even in some cases in which molecules repel each other color characteristic of the molecular interaction is produced. Methyl-4,6,4',6',-tetranitrodiphenate and mesitylene, for example, separate into two colored liquid layers; apparently a small amount of each component dissolving in the other forming some molecular compound. Hammick (55) does, however, state there is no covalent bond formation, and accepts the idea of an absorption shift of the nitro compound. This does not invalidate his criticism of the work of Briegleb.

Gibson and Loeffler (18) conclude that the nitroso group in the nitro molecule is the seat of the observed absorption since nitrosobenzene is at least as capable of bringing about deep color with aromatic hydrocarbons as is nitrobenzene, and since the absorption shift would have to be too large if the hydrocarbon were responsible. Hydrocarbons such as benzene and toluene, the hydrocarbons which would have the greatest shift, would have an absorption shift of 1500 Å., but it is observed with anthracene-tetranitromethane and acenaphthene-tetranitromethane that the shift in absorption is this great, no matter which compound is affected. The possibility that it is a shift in the absorption of the hydrocarbon cannot be ruled out for the reason given by Gibson and Loeffler.

Pauling (20) ascribes color to the stabilization of color-producing separation of charge resonance structures of the molecule. This stabilization is brought about by the effective increase in the dielectric constant caused by aromatic hydrocarbon molecules, since the coulombic force between separated charges is inversely proportional to the dielectric constant. The effective increase in dielectric constant is due to the large polarizability of the donor molecules.

According to Pauling, picric acid owes its color to the structures which have a separation of charge. There is some dispute in the literature as to whether or not pure undissociated picric acid is colored, but the assumption of Pauling that it is colored is consistent with the inability of the present author to obtain colorless picric acid. In Table 1 in the experimental section it is seen that there is some absorption by picric acid at the lower edge of the visible region when it is dissolved in carbon tetrachloride. It is difficult to believe that the picrate ion could be responsible for absorption in such a solvent; it can only be concluded that undissociated picric acid is faintly yellow, indicating the ideas of Pauling may be correct.

A decision as to the origin of the color of molecular compounds must rest upon the nature of the compounds, each theory of interaction affording a different theory of color. It is not possible to use color as a means of deciding between the covalent, ionic, and polarization theories. If it can be shown that one of the proposed theories is the correct one, then the corresponding color theory must be accepted.

There apparently has been no work on the infrared absorption of molecular compounds. Studies in this region of the spectrum could prove fruitful, as it seems likely intermolecular vibrations, which could be measured in the infrared region, would be dependent upon the nature of the interaction.

In general, the amount of interaction in solution is found to be small, and is most often estimated quantitatively by the amount of color produced. Hunter and coworkers (51) conclude that the extent of interaction (in several typical molecular compound systems) is at the most very small. However, examination of their data shows that the interaction in, for example, the naphthalene-picric acid system may be fairly large. They suggest that the deviations observed are of the same order of magnitude as deviations expected from a change of solvent. The inference that the observed effect is a solvent effect is probably not true, but the work of many others confirms the idea that the amount of molecular compound formed in solution is small.

Further discussion of the use of color in making quantitative measurements is given in the section on equilibrium measurements.

5. Equilibrium measurements on molecular compounds in solution. The problem of determining the position of the equilibrium in the interaction which forms molecular compounds has been the subject of wide interest. Although there are some who prefer other criteria, it is generally assumed that the equilibrium constant may be used as a measure of the stability of molecular compounds. Although workers who advance one of the polarization theories imply that calculated equilibrium constants have no meaning, a search of the literature reveals that no one states flatly that there are no true equilibrium constants.

a. Reversibility. There is no doubt, however, that the molecular interaction is reversible. Gibson and Loeffler (18) cite a few proofs: (1) Mixtures of aniline and nitrobenzene give a deep color; if dilute hydrochloric acid is added the color disappears, apparently because the anilinium ion is formed. If the acid is removed, the deep color returns. (2) If the aniline-nitrobenzene mixture is frozen, the color disappears, but returns upon melting. There is also other evidence in the literature to prove reversibility.

b. The problem of true equilibrium. It may be that these reversible interactions do not represent true equilibria, a problem which is not discussed adequately in the literature. Those who assume that true equilibrium exists apparently do not give much consideration to any other possibility, and those who seem to doubt that a true equilibrium exists do not give a discussion of the problem. Experimental results are given in the literature with the assumption that the answer to this question is known. Experimental results intended to decide this question are given in this paper, and the conclusion is reached that there is a true equilibrium.

Gibson and Loeffler (18) explain the phenomena observed for so-called molecular compounds without assuming a small amount of chemical compound formation. By a chemical bond they mean a covalent bond. They discuss neither the possibility of an ionic bond nor equilibrium constants. However, they do state that only a certain fraction of molecules take part in the interaction at a given moment. Whether or not this fraction can give a true equilibrium constant would seem to be an important question. They merely describe the interaction without discussing their "probability of interaction" in a quantitative manner, as an inductomeric polarization. Although they do not make themselves clear on this point, apparently they consider the interaction to be one that is stronger than ordinary dipole interactions. If they mean that the interaction is a dipole interaction, and that, therefore, no equilibrium constant is calculable, then the data presented in this paper is not in agreement with their postulate. These data show an equilibrium constant which is constant over a very wide range of concentration.

There are two other difficulties which may arise even though the calculated equilibrium constant appears to be a true one. There may be a difficulty similar to that encountered with strong electrolytes for which an apparently consistent dissociation constant can be calculated, although in actuality dissociation is complete at all concentrations. This anomaly arises from the use of concentrations instead of activities for strong electrolytes, since even in fairly dilute solutions the electric field surrounding each ion is large. In the molecular interactions studied, this difficulty does not arise because the components--except in some special cases--are always non-electrolytes dilute enough so that concentrations may be substituted for activities, and the molecular compound (or its ions) produced is so dilute that substituting concentrations for activities is permissible, even if ions are formed. Since it seems likely that concentrations may be used to calculate an equilibrium constant, it is probable that the constant obtained is a true one.

The other difficulty which may lead to a false conclusion from the constancy of the calculated equilibrium constant concerns a change in the constant measured spectrophotometrically with a change in the wavelength. This might arise if the shift in absorption of, for example, the nitro molecule depended upon the degree of interpenetration of the interacting molecules, and if this degree of interpenetration were not always the same. Then the pairs of molecules which penetrate each other most would give absorption at the lowest wavelength and, since such interpenetration would be least likely, the lowest intensity. The experimental facts show an absorption completely different from this, and the equilibrium constants calculated (given in the present work) do not vary with wavelength. This possibility of a change in equilibrium constant with wavelength is ignored by those who use color to calculate the constant, as in almost all cases the values given are obtained at only one wavelength.

Gibson and Loeffler (18) attempt to prove their polarization mechanism by studying the effect of pressure and heat on the color produced by molecular compounds. They find that the color increases with increase in pressure at constant temperature. The color increases with increase in temperature if the pressure is increased in such a way that the volume is held constant. The color increases or decreases with an increase in temperature at constant pressure; the tendency to decrease with an increase in temperature is smaller at higher pressures. All these measurements were made on mixture of pure liquids such as nitrobenzene and aniline. They assume a picture of the liquid state (56-59) in which one molecule oscillates in a cage of stationary molecules. They show that their experimental results are consistent with their theory of liquids. However, these results can also be consistent with a kind of interaction in which a true equilibrium constant may be calculated. Weiss (22) states, assuming the ionic theory, that they really measure the effect of pressure on the equilibrium

$$A + B \longrightarrow (AB) \rightleftharpoons A^+ + B^-$$

The phenomena noted above may all be explained in terms of some kind of equilibrium:

(1) Even though there is an increase in volume on mixing, the interaction in which AB is formed may in itself cause a decrease in volume, and this would have a positive pressure coefficient.

(2) The increase in absorption as the temperature is increased at constant volume may also be considered as an increase in color with an increase in pressure at constant volume. Increasing the temperature at constant pressure causes the amount of interaction to decrease slightly while increasing the pressure at constant temperature markedly increases interaction. Noting changes at constant volume merely combines these two effects, and it is to be expected that the larger effect of pressure predominates.

(3) The temperature effect on color at constant pressure may be the resultant of several effects, as is discussed more fully in the section on the heat of reaction. Either a positive or a negative temperature coefficient is possible if there is equilibrium established.

None of these phenomena permit a decision on the nature of the molecular interaction. The first two above are consistent with the polarization theory and the theories that presume a chemical equilibrium. The third may be inconsistent with the polarization theory that Gibson and Loeffler postulate, but it is not inconsistent with all polarization theories.

c. Methods of obtaining equilibrium constants. (1) Hammick and coworkers (39,49) have obtained quantities which are proportional to equilibrium constants. They do this colorimetrically for the equilibrium $A + B \rightleftharpoons C$; the equilibrium constant may be expressed by:

$$k = \frac{\frac{c}{v}}{\left(\frac{a-c}{v}\right)\left(\frac{b-c}{v}\right)}$$

where a,b represent the initial number of moles of A and B in volume v and c/v represents the equilibrium concentration of the molecular compound C. Then;

$$k = \frac{c}{(a-c)(b-c)}$$

and

$$\left(\frac{\partial c}{\partial b}\right)_{a,v} \doteq \frac{a-c}{a+b-2c+v/k}$$

If the amount of molecular compound is small, then $c \ll a$; k is small, and, therefore $v/k \gg a+b-2c$. Then, by approximation:

$$\left(\frac{\partial c}{\partial b}\right)_{a,v} \doteq \frac{ak}{v}$$

Since

$$d = Elc/v$$

where d is the optical density, E is the extinction coefficient of the molecular compound, and l is the cell thickness,

$$\left(\frac{\partial c}{\partial b}\right)_{a,v} = \frac{v}{El} \left(\frac{\partial d}{\partial b}\right)_{a,v} = \frac{ak}{v}$$

Rearranging:

$$\left(\frac{\partial d}{\partial b}\right)_{a,v} = \frac{akEl}{v^2}$$

This last equation is slightly different in their paper (49) due to an algebraic error which Hammick acknowledges in a later paper (39). Thus, if several different solutions of A and B are made in such a way so that b varies while a and v are constant, plotting d vs. b should give a straight line whose slope involves the product of k and E, as well as known constants.

Hammick and coworkers report kE for molecular compounds involving tetranitromethane and many aromatic hydrocarbons. They assume that the extinction coefficient is approximately the same for the various molecular compounds they report, and that the kE values are then indicative of relative stability in the same way that equilibrium constants indicate stability. Discussion of these relative stabilities is included in the section on the nature of the donor and the acceptor molecules.

The assumption that the extinction coefficient does not vary from one molecular compound to another when the aromatic hydrocarbons may be substances as dissimilar as benzene and β -methylnaphthalene should be, but is not, proved. In order to show that this assumption is logical they compare their relative stabilities with equilibrium constants reported by Dimroth and Bamberger (discussed below) for the molecular compounds of some of the same hydrocarbons with picric acid. Even if the work of Dimroth and Bamberger in itself were not open to serious criticism, the use of such an analogy would permit only the most general of conclusions to be made. It is likely that picric acid and tetranitromethane would act in the same way, but is better to prove this than to assume it. According to them this treatment is necessary because equilibrium constants are not obtainable. It is shown later in this paper that they are obtainable, and their assumption concerning the constancy of the extinction coefficient is compared with the results obtained in this work. Only in a very general way may their relative stabilities be accepted.

In the above derivation it was assumed that a small amount of molecular compound is formed. Only in such cases, if d is plotted against b, is a straight line obtained. A non-linear curve is reported for the mesitylene-tetranitromethane compound, and they derive an equation which may be used in this special case:

$$\frac{\partial\left(\ln \frac{\partial d}{\partial b}\right)}{\partial b} = \frac{-k}{v}$$

Here the equilibrium constant is obtainable if a plot of $\ln \frac{\partial d}{\partial b}$ vs. b gives a straight line. For mesitylene it does give a straight line, and the equilibrium constant they report is 0.07. For the concentrations given this gives a value of c which is about three percent of b and about two-tenths of one percent of a; apparently c is small enough to meet the conditions of the first derivation and the authors are greatly in error for some reason. They report complexes of tetranitromethane with naphthalene, β-methylnaphthalene, 2,4-dimethylnaphthalene, and β-naphthol which have a much greater relative stability measured by kE, than the mesitylene compound and they do not find it necessary to give these compounds the special treatment given to the mesitylene compound.

The concentrations they use are usually very small, but with the benzene-tetranitromethane compound the concentration of benzene varies from 0.70 M to 2.78 M; the tetranitromethane is 0.42 M. In the present work tetranitromethane-benzene mixtures of similar concentrations in carbon tetrachloride, the solvent which Hammick uses, are studied, and it is found that no simple relation such as the one they assume exists. It may be that concentrations may not be substituted for activities in solutions as concentrated as these. It is difficult to understand how these workers are able to obtain a straight line when plotting d vs. b in solutions concentrated with respect to benzene.

One of the aromatic hydrocarbons they use with tetranitromethane is hexamethylbenzene. In the present work data for the same two components in the same solvent, carbon tetrachloride, show that after the color is produced, it diminishes in intensity rapidly enough so that its intensity is about half its original value in twenty-four hours. It is difficult to imagine that any impurities could bring about such a loss of color, or in the case of the compounds Hammick uses, such a prevention of loss of color. This puts the work of Hammick in further doubt. Among those using colorimetric methods are von Halban and Zimpelman (44) who determine equilibrium constants colorimetrically for several systems involving acenaphthene and anthracene with a few aromatic nitro compounds.

(2) The solubility of the components and of the molecular compound formed has been used to determine the equilibrium constant by Behrend (60), Kuriloff (61), and Bamberger and Dimroth (38). Bamberger and Dimroth determine the concentration of free picric

acid in water in equilibrium with the other compound and the molecular compound formed. Weiss (22) points out that they really assume, in calculating an equilibrium constant, that Henry's Law holds for each component and the molecular compound formed. This, says Weiss, is not true for picric acid because it reacts with water. It is also true that some saturated solutions may be such that concentrations cannot be substituted for activities.

(3) Moore, Shepherd, and Goodall (40) mixed aromatic hydrocarbons with picric acid in the solvent chloroform and determined the free picric acid by noting its concentration in a water phase in equilibrium with the chloroform phase. (This requires knowledge of the distribution coefficient of picric acid between water and chloroform.) Hammick and Young (49) point out that this method measures not only the chemical effect which causes color, but also dipole effects, introducing error into the results.

(4) Brown (62) determines the equilibrium constant of naphthalene-picric acid and naphthalene-s-trinitrobenzene in nitrobenzene as solvent by measuring the freezing point depression.

(5) Brönsted (63) reports the free energy of reaction obtained from electromotive force measurements. Bronsted made measurements on the system naphthalene-picric acid-KCl-HCl-water. The

measurements are made with solid naphthalene and picric acid.

6. *The heat of formation of molecular compounds in solution*. When components are mixed to form molecular compounds, there is a heat effect. For example, this can be observed in dilute solution by measuring the temperature coefficient of color. The heat effect is of the order of magnitude of two kilocalories per mole.

Weiss (22) points out that the heat of interaction is actually a very complex quantity; he shows that if ions are formed, the heat of formation of the molecular compound AB, ΔH is given by the exact equation:

$$\Delta H/ = -Q_A - Q_B + Q_{AB} - I_A + E_B + U_c + U_p + U_D - U_R$$

where the Q terms refer to the heats of solution of A, B, and AB; I_A is the ionization potential of the donor molecule, and E_B is the electron affinity of the acceptor molecule (both in the gaseous state); U_c is the coulombic attraction energy; U_p is the energy due to polarization forces; U_D is the energy due to dispersion forces, and U_R is the repulsion potential. Weiss is incorrect in stating that the formation of molecular compound increases with an increase in temperature. He seems to be confused in the signs of ΔH and the Q terms.

If measurements were made in the gaseous state, the first three terms would be omitted, but prediction of the heat of formation would still be very difficult. Weiss criticizes the measurement Briegleb (discussed below) makes on the heat of formation in solution because it loses its significance when complicated by the heats of solution. However, measurement in inert solvents, such as carbon tetrachloride, which Briegleb often uses, should remove this difficulty because then the three Q values are probably small enough to be neglected.

Experimentally, it is shown to be true by Hammick and Yule (19) that if a solvent is not inert ΔH values are affected considerably. They use a spectrophotometric method along with the determination of Ek values discussed in the section on equilibrium measurements. They measure the optical density (used to determine k values, also) at different temperatures, and they apply the equation

$$\frac{\partial\left(\ln\left(\frac{\partial d}{\partial b}\right)\right)_{a,v}}{\partial T} = \frac{\Delta H}{RT^2}$$

derived in earlier paper (49). In this derivation they assume that there is no appreciable change in the volume of the solvent over the range of temperature with which they are concerned, 15-60° C. This is not warranted at all, and it probably introduces an error, since the change in optical density due to the change in the amount of molecular compound formed at the different temperatures is small.

Hammick and Yule report ΔH values for tetranitromethane with naphthalene, α-methylnaphthalene, and β-methylnaphthalene and for diphenylamine with mono- and dinitrochlorobenzene; all these are measured in several solvents; some are measured in as many as ten solvents. The four inert solvents are carbon tetrachloride, ethylenedichloride, n-hexane, and tetrachloroethane, which all have low dielectric constants. In all cases the heat of formation is negative, as expected. The reaction is exothermic. The six polar solvents are methylphenylketone, cyclohexanone, acetone, n-propyl alcohol, ethyl alcohol, and methyl alcohol; in all cases ΔH is more positive than in the inert solvents. Where tetranitromethane is the nitro molecule all ΔH values are positive; in the diphenylamine systems all ΔH values are negative, but are less negative than when measured in the inert solvents. Hammick and Yule offer an explanation of the solvent effect.

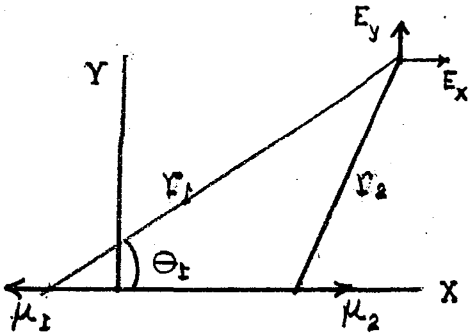
An explanation of non-solvent terms in the expression for ΔH is of greater interest. While Weiss discusses the theoretical value in terms of his ionization theory, Briegleb (17) actually calculates the energy of interaction assuming that the interaction is one in which a permanent dipole (of the nitro molecule) induces a dipole in the polarizable aromatic hydrocarbon.

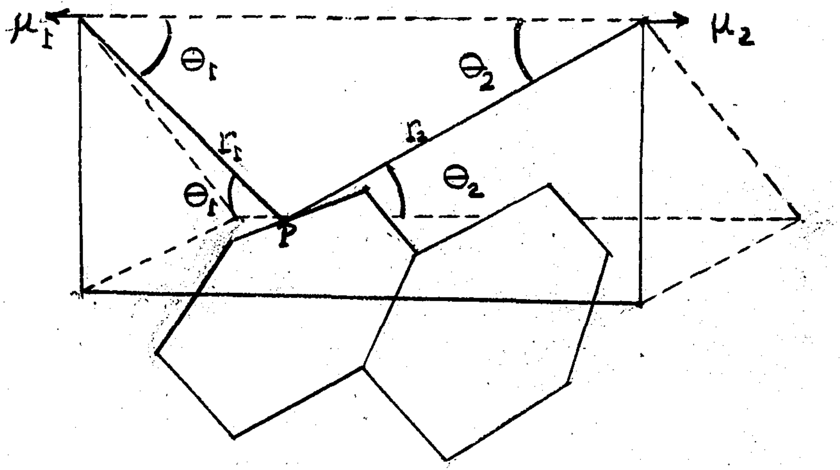
This is described in some detail for the interaction between p-dinitrobenzene and naphthalene. He assumes that the two planar molecules lie superimposed one on another in parallel planes about 3 Å. apart. This distance is about twice the so-called "radius of action" of the carbon atom; the regions of action of the two molecules thus are assumed to touch one another.

The induction energy, ΔH, for this interaction is given by:

$$\Delta H = \frac{\alpha}{2} E^2$$

where α is the polarizability of the carbon-hydrogen bond (0.65×10^{-24}) or of the carbon-carbon bond (1.06×10^{-24}), and E is the field set up by the dipole. α is calculated from a knowledge of the index of refraction; E is calculated from a knowledge of the permanent dipole moment one nitro group gives to p-nitrobenzene and from geometrical considerations. This is discussed with the aid of adjacent figures. The effect of the two nitro groups on each bond in the hydrocarbon is calculated, and the sum of all such effects is the interaction energy which is the same as the heat of reaction in the gaseous state.





The figure on the left is a planar representation of the quantities involved in the polarization of one naphthalene bond as shown on the right. All the distances and angles are known if the interplanar distance of 3 Å. is assumed; values must be known. E_X and E_Y, the components of E, may then be calculated:

$$E_X = \frac{\mu}{r_1^3}(3\cos^2\theta_1 - 1) - \frac{\mu}{r_2^3}(3\cos^2\theta_2 - 1)$$

$$E_Y = \frac{3\mu}{r_1^3}\sin\theta_1\cos\theta_1 + \frac{3\mu}{r_2^3}\sin\theta_2\cos\theta_2$$

(These equations are the corrected ones reported in errata, Z. phys. Chem., B27, 474 (1934).) The sum of the ΔH values obtained is the energy of interaction.

The interaction energies Briegleb obtains in this way are of the same order of magnitude as those he obtains spectrophotometrically; the predicted value differs from the experimental value by as much as fifty per cent. As predicted, compounds which have a higher α (polarizability) value bring about an interaction that evolves more energy.

The general agreement which Briegleb obtains between calculated and experimental values is no proof of his polarization theory. This might be sufficient proof if his calculated values were very close to the experimental values. The absolute values of the energy of interaction are all small and it is difficult to differentiate between the effect of change of solvent, the heat of reaction (if there is a chemical reaction), and the interaction energy of the polarization effect (if the polarization theory holds). It is very likely that similar values for the energy of interaction could be calculated on the basis of the other theories. For example, Briegleb shows that the energy of interaction increases, as the polarizability of the hydrocarbon increases, which agrees with experimental results. A detailed analysis of the quantities in Weiss' equation for ΔH (see above) would reveal that several of these quantities would be greatly affected in changing from a less to a more polarizable hydrocarbon (such as proceeding from benzene to naphthalene). Briegleb admits that due to the difficulty introduced by omitting the heats of solution, the absolute values are not significant. He gives meaning only to the changes noted with a change in one component. It is likely, as Hammick and Yule (19) point out, that the energy of interaction is far too small for an ordinary (presumably covalent) bond length of 1-2 Å.; the force involved varies with the reciprocal of the power of the distance, and this requires a much greater bond energy for a bond of such a length.

Instead of the energy of interaction Gibson and Loeffler (18) discuss the color coefficient of temperature. According to thermodynamics, the heat of reaction for the formation of the compound is negative if the equilibrium constant for compound formation, of the color produced, decreases with an increase in temperature; this decrease must be independent of the corresponding volume change of the solvent. By considering the structure of the liquid, they explain that the color coefficient of temperature may be either positive or negative. They postulate a cage of stationary molecules containing an oscillating molecule of the other component which produces color when it collides with the wall of the cage. Increasing the temperature at constant pressure has two effects: the "free volume" of the oscillating molecule increases and the number of collisions decreases, while the kinetic energy of the oscillating molecule increases and the number of collisions is proportional to the intensity of the color produced. If the temperature coefficient of color at constant pressure is positive, the latter effect predominates; if it is negative, the former predominates. This theory is made more plausible by showing that if the volume of the solvent is kept constant (by increasing the pressure from 1 to 1000 bars) while the temperature is increased from 25° to 85°, the temperature coefficient of color is always positive, as contrasted with the variable nature of the temperature coefficient when the pressure is kept constant.

These phenomena may be explained by both the polarization and the chemical reaction theories. Other experimental findings reported in this work and supported by similar evidence in the literature, are evidence against the polarization theory of Gibson and Loeffler. If there is a chemical reaction, it may be accompanied by a decrease in volume and an evolution of heat. It also may be that the effect of increased pressure which Gibson and Loeffler use to maintain constant volume greatly offsets the corresponding increase in temperature. This would explain why they always obtain a positive temperature coefficient at constant volume, which is the same as a positive pressure coefficient at constant volume.

But it may also be that the effect of increased pressure does not offset the effect of increased temperature and that the color coefficient of temperature is negative at constant volume. No data of Gibson and Loeffler show this, but the possibility exists from chemical reaction theory. The heat of reaction data in this paper show that such situations do exist. The volumes of the solutions studied are not kept constant, but a correction is applied so that the heat of reaction reported is that for constant volume. The heat values obtained are usually negative, corresponding to a negative temperature coefficient of color at constant volume. The heats of reaction Briegleb and others report are often -3 or -4 kilocalories; the correction for the change of volume of the solvent over the temperature interval used (usually less than thirty degrees) would not be sufficient to change the sign of the heat of reaction. A negative heat of reaction under these conditions is not possible according to the theory of Gibson and Loeffler.

There is a question as to whether or not the relative heat of reaction values are a measure of the stability of the compound or the polarization aggregation formed. It is certain that the experimental error involved is much larger in the heat measurements than in equilibrium constant measurements. Often the former values lose their meaning when they are compared with one another, the limit of error being too large. Free energy, or equilibrium constant, measurements are also more significant because they take into account the entropy changes accompanying reactions. The necessity for such a treatment in equilibrium calculations for molecular compound associations is noted by Iler (64).

Others, as von Halban and Zimpelman (44) report values of the heats of formation of molecular compounds from color data.

7. Electrical and magnetic properties of molecular compounds. a. Dipole moments. One of the principal arguments for the ionic theory offered by Weiss is the existence of dipole moments of certain molecular compounds. If molecular compound formation consists of an electron transfer, this should give rise to a permanent dipole moment in the molecular compound. Since the molecular compound and its components are slightly soluble in solvents used and the amount of molecular compound formed is very small, it would seem likely that no measurable moment would be observed in solution.

Weiss (22) reviews the subject and points out that several workers are able to make significant measurements under more favorable conditions (16, 65,66,67). s-trinitrobenzene and p-dinitrobenzene are each dissolved in carbon tetrachloride and chloroform. In all cases there is no permanent dipole moment. Each of these same two nitro compounds is also dissolved in benzene and molten naphthalene; in all cases μ is between 0.7 and 1.0 Debye unit.

b. Ions in solution. Possible evidence for the ionic theory is available from the electrical properties of certain solutions of molecular compounds. If the ionic theory holds, solutions of molecular compounds should have a measurable conductance if an ionizing solvent is used, and if the amount of molecular compound formed is fairly large. Several such observations are recorded.

Kraus and Bray (68) show that both s-trinitrobenzene and dinitrobenzene dissolve in liquid ammonia to give a deep color. Apparently ammonia is a donor molecule and colorless $(NH_3)^+$ forms. The nitro compound accepts an electron causing the deep color. Garner and coworkers (69,70) show that these solutions may be electrolyzed with migration of the nitro anion to the anode. They also show by measuring the color that the conductivity is proportional to the ion concentration, if the ion concentration may be measured by the color produced. This proves that some nitro compounds which form molecular compounds with aromatic hydrocarbons and amines, form ionic molecular compounds with liquid ammonia.

Weiss (22) reports he is able to prepare a deeply colored compound of s-trinitrobenzene and other nitro compounds with alkali metals like potassium and sodium by making an ether solution of the nitro compound with the finely divided alkali metal.

It is also possible to show that the donor molecules can form positive ions under favorable conditions. Walden (71) shows that anthracene dissolves in liquid sulfur dioxide to give a yellow color to a solution that has measurable conductivity. He also shows that some amines have a much deeper color in liquid sulfur dioxide, and that the equivalent conductance of the amine solution is much higher than that of an anthracene solution at similar concentrations. The difference in the conductivity is due to the difference in the number of ions formed. In these solutions the SO_2 molecule accepts an electron; in anthracene solutions the $(C_{14}H_{10})^+$ ion forms.

Weiss (22) points out that such aromatic hydrocarbons can also accept an electron from a metal. Compounds as anthracene and naphthalene can form addition compounds with sodium or potassium. Thus, these hydrocarbons are amphoteric.

Several salts of aromatic hydrocarbons have been prepared. In all cases the hydrocarbon molecule becomes the cation. Weiss (72,73) prepares anthracene perchlorate. The composition of anthracene perchlorate is proved by elementary analysis. It is dark brown, conducts current in and is very soluble in acetone, and there is a deposit at the cathode in electrolysis. Other salts reported are the perchlorates, sulfates, and pyrophosphates of coronene, 1,2-benzperylene, 3,4-benzpyrene, and anthracene.

None of the above evidence is for the class of molecular compounds discussed in this paper. It is true that solutions of naphthalene with picric acid and anthracene with s-trinitrobenzene dissolved in liquid sulfur dioxide have a measurable conductivity, but it is possible that this is due to the reaction of the hydrocarbon molecule with the solvent.

These facts show that the ions postulated by Weiss for molecular compounds can form under favorable conditions. The evidence for the formation of such ions in inert solvents is not sufficient. It cannot be supposed that the existence of these ions in ionizing solvents, such as liquid ammonia and liquid sulfur dioxide, proves their existence in inert solvents. Hydrogen chloride, for example, is covalent when dissolved in benzene, but largely dissociates into ions when dissolved in water. However, the existence of these ions under certain conditions shows that they may exist in inert solvents.

c. Magnetic susceptibility of solid molecular compounds. Kronberger and Weiss (30) state that if

π electrons are transferred in molecular compound formation, the magnetic suseptibility of the compound is less than the sum of the magnetic suseptibilities of the components; this is a negative deviation. They relate the same phenomenon to a decrease in polarization. With the formation of s-trinitrobenzene-perylene there is a great decrease in magnetic suseptibility. (Positive deviations are possible; there is a slight increase with the formation of quinhydrone, the molecular compound formed by the addition of quinone to hydroquinone (74,75).)

According to Kronberger and Weiss, these results are predictable from polarization measurements. Sahney and coworkers (21,76) report the magnetic susceptibility of many molecular compounds and their components; the nitro compounds are s-trinitrobenzene, 2,4-dinitrophenol, and 2,4-dinitro-1-chlorobenzene; some of the donor molecules are naphthalene, phenanthrene, anthracene, α-nitronaphthalene, α-naphthol, and aniline. Of the twenty-one molecular compounds reported, sixteen have large negative deviations; one molecular compound, benzidine-s-trinitrobenzene, has no deviation; and 2,4-dinitro-1-chlorobenzene with β-naphthol, α-naphthylamine and aniline; 2,4-dinitrophenol with aniline have positive deviations. For example, the magnetic susceptibility of naphthalene is 91.77×10^{-6} units; of s-trinitrobenzene, 74.81 x 10^{-6} units the sum is 166.58 x 10^{-6} units, and the observed value for the molecular compound is 163.03 x 10^{-6} units, a decrease of 3.55 x 10^{-6} units. The largest decrease, 14.19 x 10^{-6} units is that observed for fluorene-s-trinitrobenzene; the largest increase, 17.93 x 10^{-6} units is that observed for aniline-2,4-dinitro-1-chlorobenzene. There is no noticeable trend among the deviations; they appear to be distributed between the two extremes in a random manner.

Sahney and coworkers interpret these results in terms of the various resonance structures of the two components. They conclude that the wide deviations from additivity indicate the differences are not due to any chemical linkage, including ionic, and that the deviations are too large to be due to weak van der Waals forces. They say that there would be no deviation if the polarization idea of Briegleb were valid. They calculate the magnetic susceptibility for each of the different resonance structures of each component according to a method outlined by Gray and Cruickshank (77). This makes it possible to determine which resonance structures predominate. If there is a positive deviation, they conclude that the most highly polarized (representing a separation of charge) resonance structures of the nitro compound which have the highest magnetic susceptibilities become the most important structures of the nitro compound when the molecular compound forms. If there is a negative deviation, they conclude that the non-polarized structures of the donor molecule, which have the lowest magnetic susceptibilities, become the most important structures of the donor molecule when the molecular compound forms. These effects take place simultaneously, but they are usually unequal. They find that deviations are parallel to the amount of "internal ionic character", or the possibility of structures in which there is a separation of charge.

They do not explain the actual nature of the bond or the nature of the interaction between the components. In neither of the papers by these workers is there a clear explanation of their theory. There is no explanation of the mechanism by which the non-polar forms of the donor molecule or the polar forms of the acceptor molecule become more important. There is an obvious need for theoretical work in the magnetic susceptibilities of molecular compounds. Their experimental results do not agree with the prediction of Kronberger and Weiss in the three places that the data are comparable. With the molecular compounds of s-trinitrobenzene with phenanthrene, anthracene, and benzidine, the magnetic susceptibility deviations are negative and the dielectric polarization deviations are positive. Kronberger and Weiss expect the two deviations to have the same sign.

d. Dielectric polarization of solid molecular compounds. The dielectric molar polarization of molecular compounds is related to the magnetic susceptibility in that it also depends upon the polarizability of the electron cloud of the molecular compound. Kronberger and Weiss (30) report the dielectric constants for some molecular compounds and their components, and they discuss the polarizations calculated from these. If there is an ionic bond, there would be two principal effects: (1) The molecule that becomes the negative ion becomes more easily polarized because of the increase in the electron cloud and (2) the molecule that becomes the positive ion becomes polarized with more difficulty because the electron cloud becomes fixed. These effects are termed the "softening" and the "hardening" effects, respectively. Kronberger and Weiss obtain polarizations for molecular compounds which are either higher or lower than the sum of the polarizations of the components; this they attribute to the predominance of either the hardening or softening effect. This is formally related to the explanation of magnetic susceptibility deviations given by Sahney (see above). It is probably presumptuous to assume that the observed deviations can only be due to the formation of an ionic bond. It must be remembered that in the few places in which molar polarization data and magnetic susceptibility data are comparable, they do not agree as to the expected sign of the deviation if the ionic theory is assumed.

8. Other properties of molecular compounds.

a. Optical rotation. Leslie and Turner (78) resolved the optically active 2,4-dinitro-2-methyldiphenyl with brucine, and they found an optical rotation of ± 18.7°. When dissolved in alcohol with benzene, conditions for molecular compound formation are favorable. They noted that the rotation decreases to ±7.8° in the presence of benzene. Hammick and coworkers (54,79) obtain the d-acid by resolution with d-α-phenylethylamine, and the rotation they observe is +89.8°. This indicates incomplete resolution in the compound prepared by Leslie and Turner. The optical rotation of the d-acid of Hammick and coworkers does not change in the presence of benzene. There is no other evidence in the literature that optical rotation changes with compound formation.

Since the mirror images in the nitro compound mentioned above result from hindered rotation, it may be that covalent bond formation would cause a decrease in rotation. It is unlikely that a donor as weak as benzene would bring about enough of an interaction to cause a measurable change in optical rotation.

According to the ionic theory there are both polar molecules and free ions. If ions predominated, no change in optical rotation would be expected.

b. Hardness. No work has been done on the hardness of molecular compounds, but it has been shown (80) that some organic crystals are similar to ionic crystals, although the relationship is complex.

C. General discussion of the problem. The major purpose of the previous discussion is to show that most phenomena cited in the literature offered in support of one particular theory of interaction can be shown either to be consistent with two or more theories, or to be applied incorrectly to the problem. There are two kinds of data available for the solution of a problem such as this. The first is chemical data (equilibrium measurements, etc.) and it is a purpose of the present work to determine some chemical data to aid in the eventual solution of the problem. The second is physical data, which include crystal structure and X-ray diffraction data, color, electric and magnetic data, and molar polarization. The position taken here is that ultimately some physical data will have to decide the nature of the interaction, but that there is not enough reliable physical evidence now available to make this decision. Some chemical evidence can aid in the solution to this problem, but it would seem that a decision concerning the nature of the chemical bond or interaction must depend upon certain kinds of physical evidence. It is possible, however, to discuss these theories and indicate what may be the eventual solution.

Probably the only theories which need be considered are the covalent, ionic, and polarization theories. There is, of course, the possibility that molecular compounds actually represent some new bond type, but here it is assumed that only these three theories need be considered.

All the covalent theories would seem to be incorrect because ordinarily bond energies much larger than those obtained for molecular compounds are associated with covalent bonds. These larger bond energies are for bonds much shorter than those determined for molecular compounds in the solid state. What is usually meant by the covalent bond cannot very well be the bond existing between the components of a molecular compound.

The ionic theory seems to be too extreme a solution of the problem in that it postulates a complete transfer of an electron in solvents which are usually non-ionizing solvents. It would seem that there is no conclusive evidence for this theory, while there may be some evidence against it. It is one thing to postulate the formation of a polar molecule, but quite another to say that this polar molecule breaks down into ions. Some evidence offered to substantiate the ionic theory does not apply to the conditions under discussion; other evidence offered could just as well be consistent with a theory postulating a polar molecule which does not dissociate into ions.

The polarization theories vary, but it may be that the actual interaction is that of the formation of a polarization aggregate which is the same thing as a polar molecule, with the shortest distance between the two components 3-3.5 Å. No one who postulates one of the polarization theories attempts to prove that a true chemical equilibrium exists in solution (Briegleb does calculate some equilibrium constants, but does not prove there is a true equilibrium). In the present work it is shown that there is such an equilibrium. Thus, if there is a polarization it is not one in which there are not specific interactions between pairs of molecules, contrary to the ideas of Gibson and Loeffler. If there were a polarization aggregate, or a polar molecule, then the calculations of Briegleb can explain the low interaction energy and the ideas of Pauling (and others) can explain the color. The existence of an equilibrium and other chemical evidence (including stability) given earlier is in harmony with the idea of Briegleb and Pauling that there are specific interactions between pairs of molecules, not general interactions, as is probably the case with the ions of strong electrolytes. Such a polar molecule would have a permanent dipole moment. It would be difficult to predict the magnetic susceptibility and the molar polarization, but there can be no definite conclusions made from the confusing data on these properties cited above.

A problem similar to the one being discussed is the nature of the interaction between iodine and benzene or benzene derivatives, discussed by Benesi and Hildebrand (81). They say that there is an acid-base reaction in the Lewis sense with benzene, an electron donor, a Lewis base and iodine, electron deficient, a Lewis acid. Substituents on the benzene nucleus which tend to increase the electron density in the ring strengthen the compound formed, as would be expected if the aromatic compound acted as a Lewis base. It will be seen that the compound formed here probably is similar to the one formed between tetranitromethane and aromatic hydrocarbons. Tetranitromethane is an electron-deficient molecule and it is possible that the polar molecule described above actually is the product of a reaction between a Lewis acid and a Lewis base.

III. THE PRESENT WORK

A. The purpose of this work. There are six principal reasons for undertaking this work.

1. The determination of the ratio of the components in the compounds. Since the methods described below used for the determination of the equilibrium constant utilize measurements made over a much wider concentration range than previously reported, it is also possible to state with greater certainty than was possible earlier the ratio of the components in the compounds. It is also possible to utilize the method of continuous variations, a method used frequently in determining the ratio of reacting substances in solution, on the color of molecular compounds. The use of this method is not reported for these compounds in the literature.

2. The determination of whether or not a true equilibrium constant exists. The question of whether or not a true equilibrium constant exists is an important one. The fact that the same constant is obtained over a wide range of concentration and other reasons cited earlier in the section on equilibrium measurements show that there is a true constant.

3. The determination of the stability of molecular compounds. The equilibrium constants which are

determined not only afford conclusions concerning the questions suggested in the first two points, but they also permit an estimate of the stability of molecular compounds to be made. This is reported for several molecular compounds; all but a few are compounds of tetranitromethane with aromatic hydrocarbons. These results are obtained from spectrophotometric measurements.

4. The determination of the energy of interaction. The energy of interaction is not useful as a measure of relative stability because the experimental error is far too large, and the entropy of reaction is ignored. It does, however, make possible an estimate of the stability of a whole class of compounds such as the tetranitromethane molecular compounds. The energy of interaction is also necessary for the calculation of the entropy of reaction.

The temperature coefficient of color at constant volume can be used to calculate the energy of interaction at constant volume, but this coefficient is used as such in the discussion of the polarization theory advanced by Gibson and Loeffler.

5. The determination of the entropy of reaction. From the equilibrium constant and the heat of reaction the entropy of reaction is calculated.

6. The determination of the ultraviolet spectra of mixtures containing molecular compounds. It is

desirable to determine the nature of the ultraviolet spectra of a few representative solutions containing molecular compounds. An appreciable change in the ultraviolet spectra accompanying molecular compound formation would be of particular interest, since it might indicate the existence of a strong interaction. Lack of such a change would indicate a weak interaction.

B. Experimental.

1. Spectrophotometry. All the results listed in the previous section are based upon spectrophotometric measurements; these were all made on a Model DU Beckman Spectrophotometer. Either Corex (glass) or silica cells which have one centimeter light path were used. Occasionally cells in a set vary so that the cells used for solutions are not identical with the cell used for the solvent alone. All the cells used have been calibrated in order that this correction may be applied.

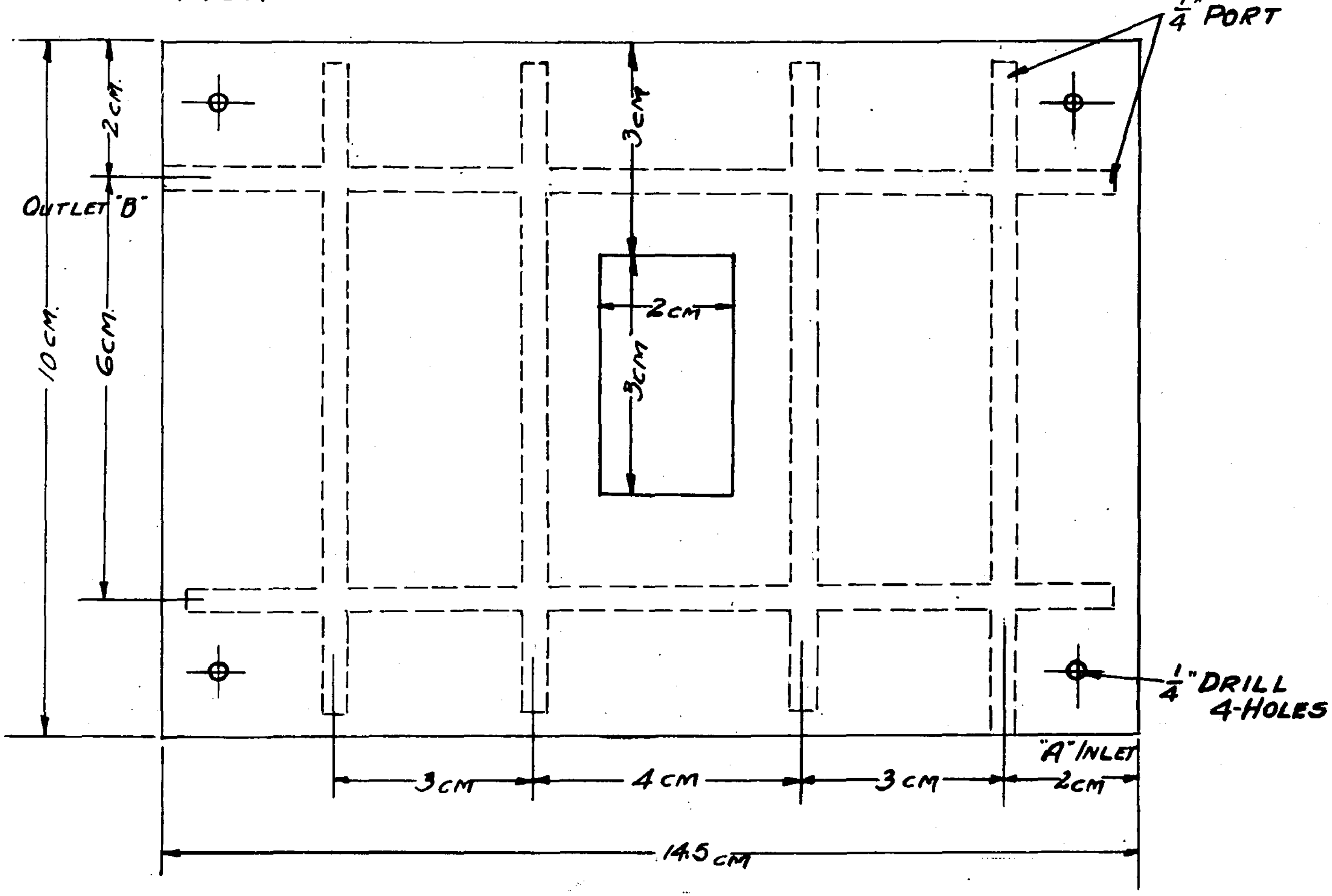
With a few systems the optical densities changed with time. The color produced by mixing hexamethylbenzene and tetranitromethane in carbon tetrachloride decreased to less than one-half its original intensity in twenty-four hours. No calculations could be made with any data of the hexamethylbenzene complex. The reason for this decrease in color is not understood, but it is probable some reaction is followed by molecular compound formation. This phenomenon was not observed by Hammick, as is mentioned in an earlier section. There was also a slow change in the optical densities of mixtures of phenanthrene and acenaphthene with tetranitromethane in carbon tetrachloride. However, equilibrium constants and approximate heats of reaction could be calculated in these cases.

Anthracene in solution slowly dimerizes in the presence of light, and the dimer is colored. This was avoided by keeping all anthracene solutions in the dark and by measuring the absorption of these solutions as quickly as possible.

To measure the temperature coefficient of color, temperature control in the spectrophotometer was necessary. A suitable attachment to the spectrophotometer was not available commercially; so one was built. One half of this attachment is shown in Figure 1. An aluminum plate, $\frac{1}{2}$" thick, was placed on each side of the cell compartment. (It is possible to insert plates such as these on the DU Spectrophotometer.) The opening in the center allows the light to pass through. Water of the desired temperature enters at A and leaves at B. The dotted lines show possible routes the water may travel. The side of the plate that faces the cells was painted black to avoid any possible light reflection. The other side of the plate was separated from the

TEMPERATURE CONTROL PLATE

FIG. 1



1.25 CM. X 10 CM. X 14.5 CM.
ALUMINUM PLATE

instrument by a sheet of asbestos for the purpose of insulation, although there is little danger that the rather small temperature differentials used would affect the instrument. Screws which connect the phototube housing to the main part of the instrument were replaced with longer screws to take care of the thickness of the plates.

The water was circulated by means of an ordinary water pump from a refrigerated bath. Since tetranitromethane freezes at 13°, and the solid is much less soluble in carbon tetrachloride, the solvent used, the temperature in the cells was kept above 13°. Usually, the highest temperature used was about 28°. Where picric acid was used the lowest temperature was about 6°.

To avoid condensation of water vapor at these temperatures, since often the dew point is only a few degrees below room temperature, the cells were kept in the cell compartment until all the measurements at all the temperatures were completed, by sealing the cell compartment, and by keeping Drierite in the cell holder in place of one of the cells. All the readings could be taken in a few hours because the bath temperature could be changed three or four degrees in about fifteen minutes. The compartment was sealed at the top by use of a weighted rubber cover and by use of stopcock grease which was used at all possible openings of the compartment.

Since the solutions were kept in the cells for a few hours, it was necessary to prevent loss of the volatile substances. As no glass stoppered cells were available when this work was done, the cells that were used had their loose fitting covers sealed on by means of a wax.

The temperature in the cells was determined by ascertaining the temperature difference between the bath and the cells at different temperatures under the conditions of the experiment. A thermometer was placed in the cells (which were then covered) and the temperature difference between the cells and the bath was noted. A 0-50° thermometer calibrated in tenths was used for all measurements. There may be a small error in the absolute values of the temperatures obtained in this way, but only the relative values are needed, and these are undoubtedly more accurate than necessary, since there is greater error in the optical densities measured.

2. Materials. The solvents used were C.P. grade. The hydrocarbons were recrystallized several times from ethanol or benzene, except 1,2-benzanthracene, which was recrystallized from a mixture of acetic acid and ethanol. Picric acid was recrystallized from water; a glass fritted filter was used to avoid the formation of addition compounds with filter paper.

The purity of the hydrocarbons was determined by the constancy of the melting point; the melting points of sucessive recrystallizations were determined simultaneously to minimize errors. All the melting points were in good agreement with those found in the literature.

The purity of the picric acid was assayed by neutralization with alkali, using methyl red as indicator (82). It was found to be slightly less than 99% pure, the impurity probably being water which could not be removed. The melting point agreed well with that found in the literature. It is certain that the small amount of water impurity would have no appreciable effect upon the optical measurements made.

The tetranitromethane used was prepared according to the method of Chattaway (83). Fuming nitric acid (the anhydrous fuming nitric acid recommended by Chattaway was found not to be necessary) was mixed with acetic anhydride and kept in an ice bath for several hours; care was taken not to agitate the mixture for several days. At the end of a week the product separated with the addition of a large excess of water. The oily liquid was washed with water and dilute sodium carbonate and dried over sodium sulfate. The product was purified by fractional distillation at 15-25 mm. of mercury at 25-30° to prevent decomposition below 125°, the boiling point.

The color of all lots was fairly yellow. Hammick and Young (49) report the preparation of colorless tetranitromethane, but recent work that has been done very carefully by Nicholson (84) shows that the colorless compound probably cannot be prepared.

Nicholson very carefully prepared pure tetranitromethane and he reports physical constants which are probably more reliable than others in the literature. The freezing point he reports, 13.8°, is higher than any other given; some are as low as 12.5°. He found that the method of preparation of Chattaway (the method used in this work) could yield a pure product only with many distillations. The physical constants of the substance he prepared by another method with very laborious purification are compared with those of the substance used in the work of the present author. The refractive index he reports at 20° for the D-line of sodium is 1.4384; for the substance of this work, all lots had refractive indices between 1.4376 and 1.4381. This is significantly lower than Nicholson's value. The density obtained by Nicholson is 1.630 g/ml. at 25°; one lot of the tetranitromethane of this work had a density of 1.622 at 25°.

The tetranitromethane prepared here was distilled in a six plate column after drying. It may be that the product was impure, but it is not believed that the results of the work are seriously affected.

Nicholson suggests that the chief impurity may be trinitromethane. It would seem that this substance would act in a manner similar to that of tetranitromethane in molecular compound formation. To prepare tetranitromethane whose purity approached that of the substance prepared by Nicholson would be prohibitively difficult, since he was only able to prepare a few samples of one milliliter each, while a few hundred milliliters were used in the present work.

The optical densities of tetranitromethane and of picric acid in the visible region are given in Table 1.

C. Treatment of the data.

1. Equilibrium constants. In order to achieve the aims set forth it is necessary to be able to calculate a true equilibrium constant over wide ranges of concentrations. The method of obtaining this constant follows.

Let the reaction

$$A + B \rightleftarrows AB$$

represent the reversible formation of a molecular compound AB from components A and B. Let c_1 and c_2 be the initial molar concentrations of A and B, respectively, and x_I the equilibrium molar concentration of AB. Then the equilibrium constant K is given by

$$(1) \quad K \simeq \frac{x_I}{(c_1 - x_I)(c_2 - x_I)} = \frac{x_I}{c_1c_2 - c_1x_I - c_2x_I + x_I^2}$$

We assume x_I, the amount of molecular compound formed, is small; this is justified, since it is found to be true with the use of this assumption. Then x_I^2 may be ignored in comparison with c_1x_I or c_2x_I, since either c_1 or c_2 or both always are much larger than x_I. Then

$$(2) \quad K(c_1c_2 - c_1x_I - c_2x_I) = x_I$$

Dividing both sides of this equation by Kx_I

$$(3) \quad \frac{c_1c_2}{x_I} - c_1 - c_2 = \frac{1}{K}$$

The optical density at a given wavelength, d, may be defined for this solution in terms of E, the molar extinction coefficient,

$$(4) \quad d_I = x_IE$$

d_I is the observed optical density when the molecular compound formed is the only colored substance. In some instances one of the components absorbs slightly in the region of interest. The absorption calculated to be due to a component is subtracted from the observed absorption. This approximation is justified because it always produced results consistent with those obtained where the correction was unnecessary.

Substituting in the above,

$$(5) \quad \frac{c_1c_2E}{d_I} - c_1 - c_2 = \frac{1}{K}$$

Solving for E,

$$(6) \quad E = \frac{d_I}{c_2} + \frac{d_I}{c_1} + \frac{1}{K}\frac{d_I}{c_1c_2}$$

d of another solution of the compounds can be measured, giving a similar equation. Then c_1 becomes c_3, c_2 becomes c_4, and d_I becomes d_{II}. Then

$$(7) \quad E = \frac{d_{II}}{c_4} + \frac{d_{II}}{c_3} + \frac{1}{K}\frac{d_{II}}{c_3c_4}$$

The right hand sides of these two equations can be equated and these two solutions can be chosen so that the concentration of A changes while the concentration of B remains constant; therefore, c_2 may be substituted for c_4. Then

$$(8) \quad \frac{d_I}{c_2} + \frac{d_I}{c_1} + \frac{1}{K}\frac{d_I}{c_1c_2} = \frac{d_{II}}{c_2} + \frac{d_{II}}{c_3} + \frac{1}{K}\frac{d_{II}}{c_2c_3}$$

Rearranging,

$$(9) \quad \frac{1}{K}\left(\frac{d_I}{c_1c_2} - \frac{d_{II}}{c_2c_3}\right) = \frac{d_{II}}{c_2} + \frac{d_{II}}{c_3} - \frac{d_I}{c_2} - \frac{d_I}{c_1}$$

Rearranging further,

$$(10) \quad \frac{1}{K} = \frac{d_{II} - d_I + \frac{d_{II}c_2}{c_3} - \frac{d_Ic_2}{c_1}}{\frac{d_I}{c_1} - \frac{d_{II}}{c_3}}$$

Dividing as shown,

$$(11) \quad \frac{1}{K} = \frac{d_{II} - d_I}{\frac{d_I}{c_1} - \frac{d_{II}}{c_3}} - c_2$$

This is one of the desired equations. When c_2 is small and K is also small, c_2 may be neglected. This is usually the case, but there is no difficulty when this approximation is not made.

The equilibrium constant could be calculated from (11) if the d values could be known with sufficient accuracy. However, in practice the difference between d_I/c_1 and d_{II}/c_3 is small in comparison to the absolute values, and so the inevitable error in the optical measurement leads to a very large error in the equilibrium constant. No consistent results were obtainable by comparing the K values obtained from different pairs of solutions.

Equation (11) could be used if d_I and d_{II} were accurately known. No improvement could be affected by taking an average of several measurements, but it was found possible to use equation (5)

$$\frac{c_1 c_2 E}{d_I} - c_1 - c_2 = \frac{1}{K}$$

to obtain more accurate values of d_I and d_{II}. Equation (5) may be rewritten

$$(12) \quad \frac{c_1}{d_I} = \frac{c_1}{c_2 E} + \frac{c_2 + \frac{1}{K}}{c_2 E}$$

If the concentration of B is kept constant while A is varied, then c_1 changes to c_3, c_5, c_7, etc, and c_2 remains constant. If c_1/d_I, c_3/d_{II}, c_5/d_{III}, etc., are plotted against c_1, c_3, c_5, etc., a straight line whose slope is $1/c_2E$ and intercept is $\frac{c_2 + 1/K}{c_2E}$ should be obtained. Since the experimental data does give a straight line under these conditions, equation (11) may be used by selecting "ideal" values of d_I and d_{II} from the straight line obtained from (12). One such linear plot is given in Figure 2. The accuracy of the data does not warrant using the tedious least squares method of obtaining the best straight line through the points that are plotted. Values from the extreme ends of the straight line were chosen to increase the differences, and hence the accuracy, in (11). The equilibrium constant was calculated from four to eleven different wavelengths for the systems studied, and the average of these values for each system was determined. The concentrations, observed optical densities, and calculated equilibrium constants are included in Tables 2-19.

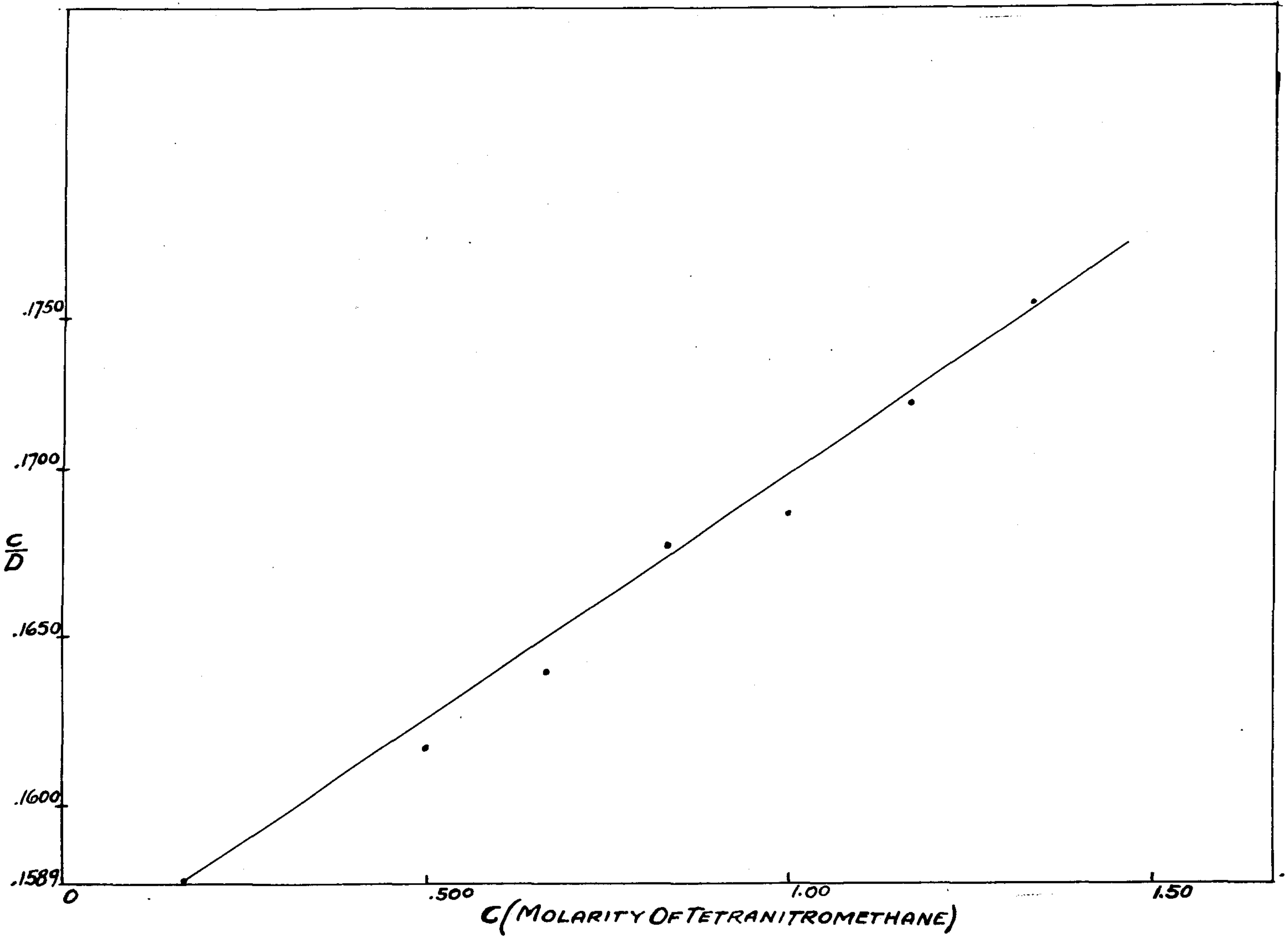
The range of concentrations used is as wide as the solubilities, usually in carbon tetrachloride, permit. The constants are determined in solutions in which one component is much in excess; six to nine different solutions are used. These solutions are made up so that the most concentrated is nine times as concentrated as the most dilute (where nine solutions are used). Where possible the same experiment was performed at concentrations such that the other component was present in excess. This could be done except with the higher condensed hydrocarbons.

In only two instances could no calculation of K be made. Concentrated benzene with dilute tetranitromethane and concentrated mesitylene with tetranitromethane give results wholly different from all other results. The amount of tetranitromethane was held constant as the benzene or mesitylene concentrations increased. Optical densities increased much more rapidly with increasing benzene or mesitylene concentration than would be expected if there were a 1:1 interaction. However, the interaction is very weak and high benzene or mesitylene concentrations (1-6 M) must be used. It is very likely that activities are very far from molarities in this range. It is also true that there is essentially a change of solvent, and change of solvent in itself affects absorption.

In Tables 2-19, containing the data for the equilibrium constants, the equilibrium constant calculated for each wavelength is given. The average of these values is also given with the average deviation. The average deviation is large because of the difficulty of using optical methods for the determination of a very small equilibrium constant.

FIG. 2

$\frac{C}{D}$ VS. C FOR CONCENTRATED TETRANITROMETHANE-DILUTE NAPHTHALENE AT 470 mμ (DATA IN TABLE 2)



An attempt to measure the equilibrium constant of 1,2-benzanthracene with tetranitromethane was made, but the low solubility of the hydrocarbon gave small optical densities. The equilibrium constants calculated for 1,2-benzanthracene vary widely and they are wholly unreliable.

The free energy of reaction, ΔF^o, is recorded in Table 32. It is calculated from the relationship $\Delta F^o = -RT\ln K$. Since K is given in all cases within a few degrees of 25^o, and the range of change of K with temperature is small, all values are assumed to be at 25^o.

2. Heat of reaction. Since the heat of reaction is related to the change of the equilibrium constant with temperature, it is possible to make measurements used for the equilibrium constant at different temperatures in order to get the heat of reaction. From (5) it is known that

$$\frac{1}{K} = \frac{c_1 c_2 E}{d_I} - c_1 - c_2$$

Rearranging,

$$(13) \qquad \frac{d_I}{K} = c_1 c_2 E - c_1 d_I - c_2 d_I$$

$$(14) \qquad K = \frac{1}{\dfrac{c_1 c_2 E}{d_I} - c_1 - c_2}$$

It is well known from thermodynamics that

$$(15) \qquad \ln K = \frac{-\Delta H}{RT} + M$$

where ΔH is the heat of reaction and M is an integration constant. Combining (14) and (15),

$$(16) \quad \ln K = -\ln\left(\frac{c_1 c_2 E}{d_I} - c_1 - c_2\right) = \frac{-\Delta H}{RT} + M$$

From this the heat of reaction may be determined, since plotting $\ln\left(\frac{c_1 c_2 E}{d} - c_1 - c_2\right)$ against $1/T$ at one wavelength gives a straight line whose slope is $\Delta H/R$. d is now a variable; it is the optical density at temperature T. The concentrations, c_1 and c_2, change slightly with temperature due to the change in the density of the solvent. These are calculated at each temperature. The density of carbon tetrachloride as a function of temperature in the range used, 5-30°, is well known and the values used are recorded in International Critical Tables. There is not general agreement concerning the density of ethylene dichloride as a function of temperature, but the values recorded at various temperatures in the literature are consistent enough to permit their use. The experimental error is larger than the error in using these density measurements.

In this way the heat of reaction determined is the heat of reaction at constant volume. The results are then comparable to those of Gibson and Loeffler, who use different conditions.

In order to make the linear plot indicated above, it is necessary to know E, the extinction coefficient of the molecular compound at the desired wavelength. It is assumed that E is constant over the small temperature range used. The value used is determined from the equilibrium constant data. Equation (6)

$$E = \frac{d_I}{c_2} + \frac{d_I}{c_1} + \frac{1}{K}\,\frac{d_I}{c_1 c_2}$$

may be rearranged to give

$$(17) \qquad E = d_I \left(\frac{\frac{1}{K} + c_1 + c_2}{c_1 c_2} \right)$$

In the equilibrium constant data d values are given for concentration c_1, c_3, c_5, etc., while c_2 is held constant. Since $1/K$ is constant, E may be determined for each d value measured at a given wavelength. The average of these values is used in (16).

The heat of reaction, or heat of molecular compound formation, is determined in each of two different concentrations at four different wavelengths for each molecular compound studied. The average of the eight values thus obtained is reported.

E values are given in Table 20. E values other than those needed for ΔH calculation are also given. ΔH values and the data used for their calculation are given in Tables 21-31.

The error in the heat of reaction is expressed in the large average deviation. The order of magnitude is all that can be significant in the heat of reaction values.

With each table in the heat of reaction calculation are given three concentrations. One is for the dilute component, and the other two are for the two different concentrations used for the concentrated component; each of these two is used for an indepenent determination of the heat of reaction. The concentrations given are for the highest temperatures given, but in the calculations all concentrations were determined for all temperatures. In the columns giving the optical densities, the first column under each wavelength gives the optical densities of the smaller of the two concentrations of the more concentrated component, and the second column gives the optical densities for the larger of these two concentrations.

3. <u>Entropy of formation</u>. From the free energy of reaction and the heat of reaction the entropy of reaction may be calculated from

$$(18) \qquad \Delta S = \frac{\Delta H - \Delta F}{T}$$

ΔS values are given in Table 32 along with the ΔF and the ΔH values. Since these quantities are all measured near 25°, and they change only slightly with temperature, T is assumed to be 298° K. in all cases.

4. The ultraviolet and visible spectrum of a mixture of the components of molecular compounds. No peak due to the formation of a molecular compound has been found. There is appreciable absorption in the visible region, and it is this absorption that is used for the determination of the concentration of the molecular compound in the calculation of the equilibrium constant and the heat of reaction. If there is a weak interaction between the components of the molecular compound, little or no effect on the ultraviolet absorption spectra would be expected. The ultraviolet optical densities of benzene, naphthalene, picric acid, tetranitromethane, and the four 1:1 mixtures which can form molecular compounds are given in Table 33. Ethanol is used as a solvent because it is transparent in this spectral region. The average of the densities of the components is also given. It is seen that the difference between the observed and the calculated (average) values becomes smaller in proceeding from the visible region to the low ultraviolet region. The difference that is usually small in the ultraviolet region may be due to experimental error. It is certain, however, that the absorption peaks in the solutions in which there is molecular compound formation are where they

are expected to be. This shows only that there is no large effect in the ultraviolet region, since the highly absorbing components account for almost all the observed absorption in the mixtures.

5. The ratio of the components in the molecular compounds. The ratio of components is assumed to be 1:1 in the calculation of the equilibrium constant and this assumption is probably correct when a plot of c_1/d_I, c_3/d_{II}, c_5/d_{III}, etc., against c_1, c_3, c_5, etc., is linear. However, further confirmation is desirable and this is made possible by the use of the "method of continuous variations" originated by Job (85) and developed by Vosburgh (86).

The method of continuous variations is applied to the determination of the ratio of the components in molecular compounds in the following manner: equimolar solutions of components A and B were mixed in varying proportions such that the sum of the volumes used of the solutions of A and of B was constant. The optical densities of these solutions were measured at several wavelengths. A plot of optical density against concentration of one component was made for each wavelength of each solution. The data for all the molecular compounds studied are in Tables 34-37. Only typical curves for each mixture are given in Figures 3-5, since the curves omitted are similar to those given.

FIG. 3
CONTINUOUS VARIATIONS FOR NAPHTHALENE-TETRANITROMETHANE AND FOR ACENAPHTHENE-TETRANITROMETHANE (DATA IN TABLES 34 AND 35)

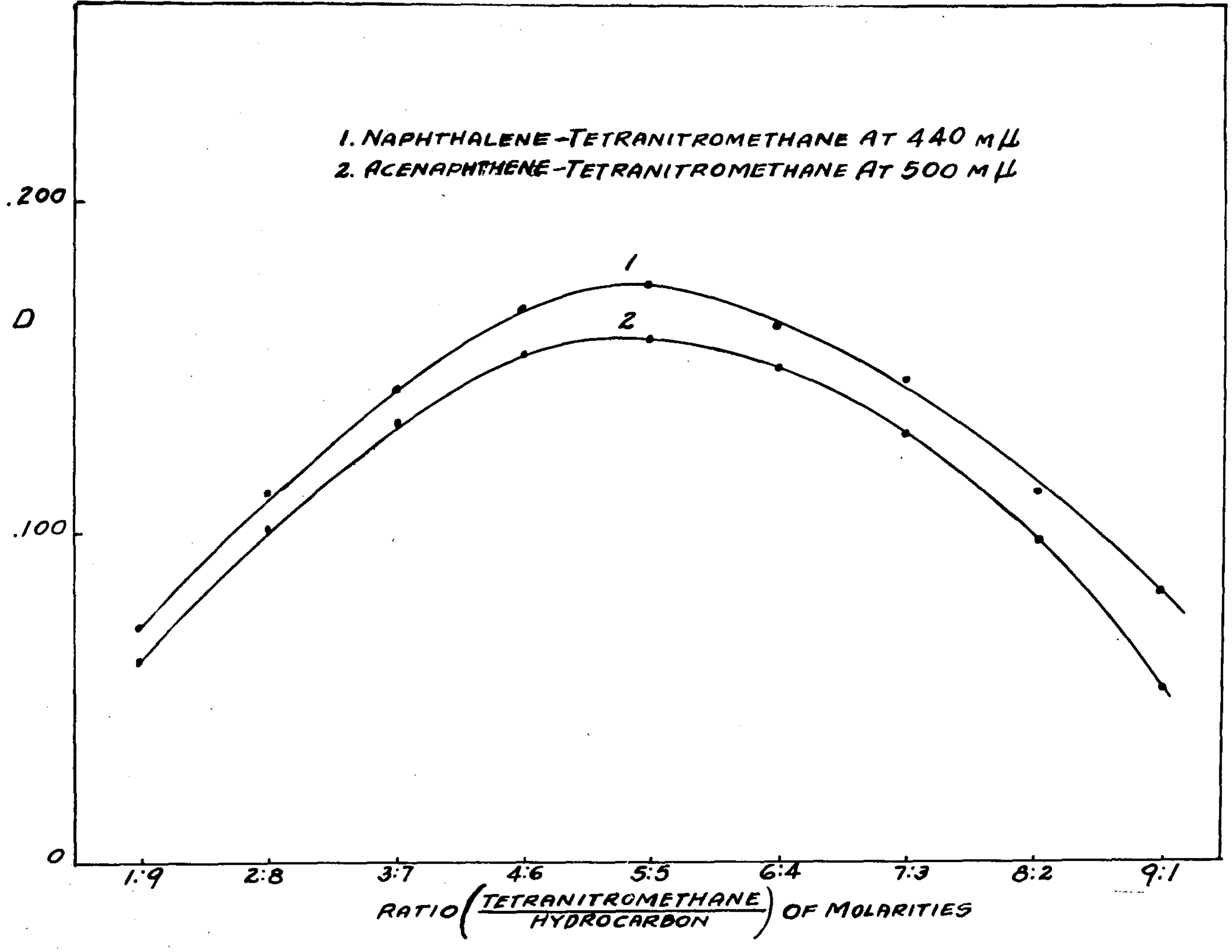


FIG. 4

CONTINUOUS VARIATIONS FOR MESITYLENE-TETRANITROMETHANE (DATA IN TABLE 36)

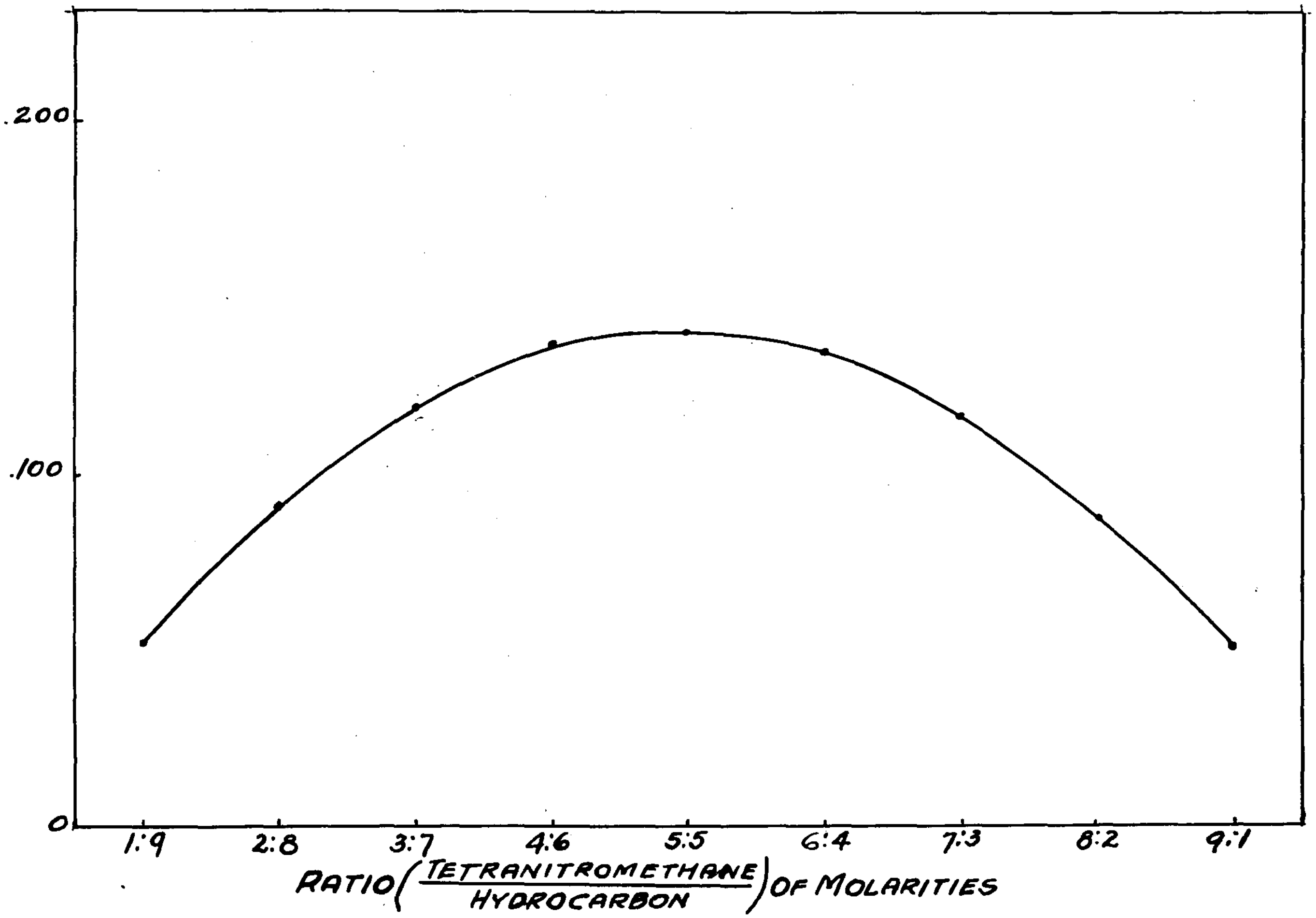
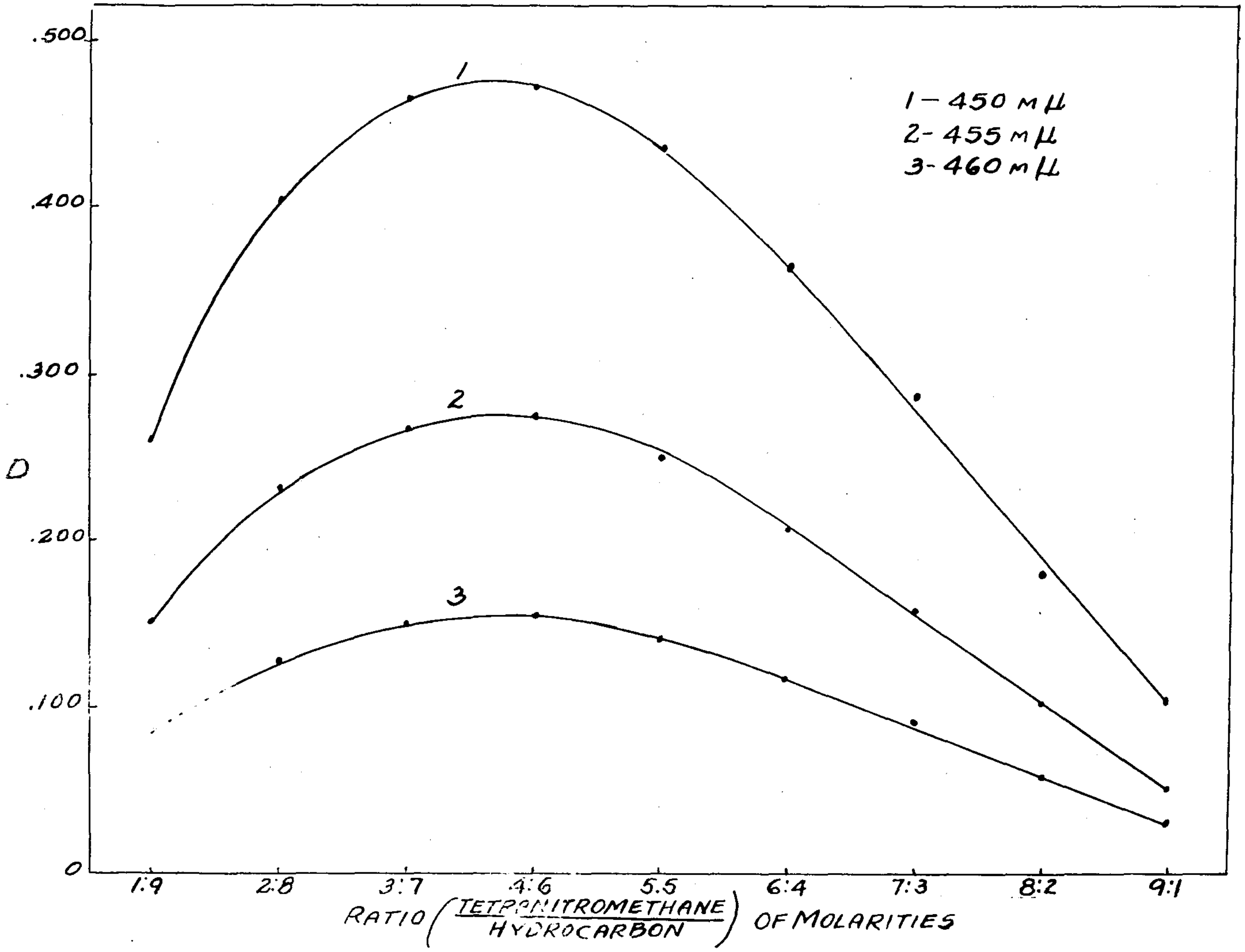


FIG. 5

CONTINUOUS VARIATIONS FOR BENZENE-TETRANITROMETHANE (DATA IN TABLE 37)



If there is a 1:1 compound formed, the greatest amount of compound, under the conditions of the experiment, will form when the concentrations of the components are equal. This is true because the smaller of the two component concentrations is the limiting factor in determining the amount of molecular compound that will form. The amount of molecular compound that forms is always a function of the equilibrium constant, but the largest amount will form when the concentrations of the components are equal. If there is a 1:2 molecular compound formed, then the maximum optical density is observed where the concentrations of the two components are in that 1:2 ratio. Other physical properties, such as refractive index, may be used in the same way in certain systems. If compound formation caused a decrease in a certain physical property, there will be a minimum in the curves plotted as described above.

If a 1:1 and a 1:2 compound are both present in appreciable amounts, the method of continuous variations cannot be used to determine this fact. The data reported here shows maximum absorption where the concentrations of the components are equal, except in the case of benzene-tetranitromethane. This exception has been discussed earlier; the reason being that the concentrations used are too high. A 1:1 ratio means that if there is only one compound formed it is of the type AB. Since it is very probable that there is only a small amount of AB present, it seems unlikely that AB reacts with B to form an appreciable amount of AB_2.

Table 1. Absorption of nitro compounds

mmu	pure tetranitromethane	4.03×10^{-3} M picric acid in CCl_4
400		.207
405	2.03	.127
410	1.194	.072
415	0.675	
420	.364	.026
425	.202	
430	.113	
435	.064	
440	.035	
445	.022	

Table 2. Spectra of dilute naphthalene-concentrated tetranitromethane Naphthalene, 6.72 x 10^{-3} m/l

mmu				C of TNM					K
	.1655	.3310	.4965	.6620	.8275	.9930	1.159	1.324	
410	.320	.614	.965	1.238	1.513	1.783	2.14	2.30	.143
420	.274	.527	.820	1.070	1.308	1.532	1.816	1.944	.162
430	.243	.464	.718	.935	1.171	1.367	1.595	1.759	.111
440	.202	.390	.608	.802	.994	1.169	1.371	1.531	.0727
450	.169	.325	.503	.662	.813	.973	1.163	1.285	.0581
460	.134	.258	.401	.525	.642	.771	.894	.993	.0854
470	.104	.197	.306	.402	.493	.589	.676	.759	.0848
480	.074	.141	.219	.288	.355	.423	.493	.553	.0596
490	.048	.093	.149	.203	.251	.301	.350	.392	.0560
500				.132	.162	.197	.224	.252	.0760
510				.087	.107	.132	.142	.161	.1404

Ave. K $\simeq$ .095 ± .032

Table 3. Spectra of concentrated naphthalene-dilute tetranitromethane Tetranitromethane, 8.28×10^{-3} mole/l.

	mmu					
c of naphthalene	410	420	430	440	450	460
0.0949	.101	.099	.091	.086	.066	.051
.1898	.193	.185	.170	.147	.125	.100
.2847	.284	.277	.253	.220	.187	.150
.3796	.382	.366	.341	.303	.255	.196
.4745	.470	.448	.421	.371	.312	.243
.5694	.554	.535	.496	.441	.373	.290
.6643	.642	.611	.574	.503	.424	.344
.7592	.733	.705	.658	.583	.487	.398
.8541	.809	.768	.722	.634	.538	.437
K	.113	.122	.140	.154	.131	.116

Ave. K = .13 ± .01

Table 4. Spectra of dilute anthracene-concentrated tetranitromethane Anthracene, 2.74×10^{-3} mole/l.

	mmu					
c of TNM	500	510	520	530	540	550
0.3310	.121	.114	.107	.100	.090	.082
.4965	.180	.172	.160	.149	.137	.123
.6620	.232	.220	.204	.191	.174	.158
.8275	.257	.244	.228	.212	.193	.176
.9330	.315	.300	.284	.264	.244	.216
1.324	.393	.372	.352	.325	.302	.269
K	.282	.322	.270	.297	.231	.270

Ave. K = .28 ± .02

Table 5. Spectra of dilute phenanthrene-concentrated tetranitromethane Phenanthrene, 1.42 x 10^{-3} moles/l.

c of TNM mmu	410	420	430	440	450	460	470
.1655 moles/l.	.127	.095	.081	.074	.064	.056	.050
.3310	.224	.165	.143	.128	.112	.098	.086
.4965	.309	.226	.194	.175	.151	.132	.114
.6620	.390	.284	.245	.217	.190	.164	.144
.8275	.461	.333	.288	.252	.221	.195	.168
.9330	.525	.377	.321	.283	.249	.216	.188
1.159	.580	.411	.352	.309	.270	.233	.202
1.324	.644	.457	.393	.345	.301	.262	.228
K	.472	.539	.595	.661	.659	.702	.652

Ave. K = .61 ± .06

Table 6. Spectra of concentrated phenanthrene-dilute tetranitromethane Tetranitromethane, 0.01655 moles/l.

c of phenanthrene mmu	430	440	450	460	470
.02322 moles/l.	.101	.087	.066	.050	.041
.03483	.136	.118	.094	.074	.060
.04644	.188	.164	.129	.099	.078
.05805	.221	.193	.155	.123	.098
.06966	.271	.237	.190	.149	.120
.08127	.313	.272	.221	.174	.138
.09288	.347	.301	.247	.195	.156
.10449	.390	.340	.277	.220	.176
K	1.306	.776	.868	.211	.453

Ave. K = 0.72 ± .31

Table 7. Spectra of dilute chrysene-concentrated tetranitromethane Chrysene, 3.93 x 10^{-4} moles/l.

	mmu				
c of TNM	420	430	440	450	460
.3310 moles/l.	.071	.067	.063	.057	.049
.4965	.090	.089	.078	.069	.055
.6620	.116	.102	.095	.084	.069
.8275	.139	.122	.110	.095	.079
.9330	.161	.136	.125	.107	.089
1.159	.175	.150	.138	.119	.099
1.324	.198	.169	.153	.132	.113
K	.315	.771	.619	.784	.632

Ave. K = .62 ± .13

Table 8. Spectra of dilute benzene-concentrated tetranitromethane Benzene, 0.337 M

	mmu				
c of TNM	420	425	430	435	440
1.324	.179	.098	.051		
1.986	.263	.150	.080	.043	
2.648	.354	.203	.104	.061	
3.310	.444	.255	.135	.078	.041
3.972	.535	.313	.165	.094	.051

No K value could be calculated; this is explained in the text.

Table 9. Spectra of concentrated benzene-dilute tetranitromethane Tetranitromethane, 0.827 M

c of benzene	mmu 430	434	440	444	450	454
1.12	.124	.079				
2.24	.307	.194	.095	.062		
3.36	.564	.365	.184	.119	.058	
4.48	.871	.575	.297	.193	.097	.061
5.60	1.228	.829	.436	.290	.152	.095
6.72	1.664	1.158	.640	.422	.226	.143
7.84		1.499	.850	.564	.309	.197
8.96		1.904	1.118	.756	.423	.275

No K value could be calculated; this is explained in the text.

Table 10. Spectra of dilute mesitylene-concentrated tetranitromethane Mesitylene, 1.44 x 10^{-2} mole/l.

c of TNM	mmu 430	440	450	460	470	480
.3310	.281	.202	.140	.090	.053	.030
.4965	.417	.301	.208	.135	.081	.047
.6620	.549	.396	.273	.174	.105	.062
.8275	.670	.483	.333	.213	.127	.076
.9330	.800	.580	.401	.255	.153	.090
1.159	.914	.660	.454	.291	.174	.101
1.324	1.023	.745	.510	.328	.196	.115
K	.110	.284	.225	.108	.171	.0751

Ave. K = 0.16 ± .07

Table 11. Spectra of concentrated mesitylene-dilute tetranitromethane Tetranitromethane, .01655 M

c of mesitylene	mmu 460	470	480	490	500
0.718	.218	.129	.072		
1.436	.451	.271	.156	.084	
2.154	.677	.415	.242	.133	.071
2.872	.901	.560	.332	.185	.097
3.590	1.151	.716	.434	.247	.134
4.310	1.407	.889	.544	.315	.173
5.025	1.639	1.030	.632	.370	.208
5.740	1.803	1.200	.751	.446	.255
6.460	2.12	1.352	.857	.515	.299

No K value could be calculated; this is explained in the text.

Table 12. Spectra of dilute acenaphthene-concentrated tetranitromethane Acenaphthene, 1.58 x 10^{-2} moles/l.

c of TNM	mmu 510	520	530	540	550	560	570	580	590
.1655	.206	.177	.147	.119	.100	.076	.060	.044	.033
.3310	.413	.355	.295	.239	.197	.150	.115	.086	.063
.4965	.618	.531	.441	.356	.292	.225	.171	.126	.092
.6620	.790	.674	.573	.467	.375	.290	.221	.165	.120
.8275	.999	.851	.721	.588	.466	.364	.278	.206	.149
.9330	1.179	1.007	.850	.692	.552	.427	.327	.243	.175
1.159	1.333	1.153	.969	.795	.634	.494	.375	.281	.204
1.324	1.508	1.305	1.089	.903	.720	.560	.424	.318	.230
1.490	1.627	1.425	1.186	.988	.780	.608	.460	.345	.249
K	.125	.0934	.0785	.0554	.1185	.0714	.1208	.0966	.1144

Ave. K = .097 ± .02

Table 13. Spectra of concentrated acenaphthene-dilute tetranitromethane Tetranitromethane, 0.01655 mole/l.

c of	mmu						
acenaphthene	460	470	480	490	500	510	520
.05270	.114	.105	.099	.089	.081	.070	.060
.1054	.230	.213	.199	.179	.162	.143	.123
.1581	.342	.318	.297	.272	.244	.216	.186
.2108	.454	.424	.389	.355	.319	.284	.245
.2635	.565	.530	.485	.450	.400	.356	.307
.3162	.677	.633	.579	.535	.476	.423	.365
.3689	.779	.724	.669	.612	.550	.486	.420
.4216	.866	.805	.745	.681	.611	.544	.466
.4743	.997	.928	.855	.783	.703	.627	.543
K	.155	.0776	.111	.0769	.1052	.0746	.0443

Ave. K = .092 ± .02

Table 14. Spectra of dilute fluorene-concentrated tetranitromethane Fluorene, 1.71 x 10^{-3} moles/l.

mmu c of TNM	410	420	430	440	450	460	470
.3310	.161	.111	.094	.080	.067	.056	.046
.4965	.224	.153	.128	.109	.091	.073	.058
.6620	.283	.191	.160	.137	.114	.091	.073
.8275	.337	.224	.188	.162	.135	.110	.090
1.159	.437	.283	.237	.203	.167	.135	.106
1.324	.482	.312	.260	.222	.185	.150	.118
K	.342	.465	.502	.479	.573	.632	.602

Ave. K = .51 ± .07

Table 15. Spectra of concentrated fluorene-dilute tetranitromethane Tetranitromethane, 0.008275 mole/l.

mmu c of fluorene	410	420	430	440	450	460	470
.0673	.115	.098	.085	.074	.063	.052	.041
.1009	.166	.143	.125	.109	.094	.077	.063
.1346	.220	.190	.163	.145	.124	.102	.083
.1682	.267	.234	.203	.180	.152	.125	.104
.2019	.315	.276	.242	.213	.182	.151	.124
.2355	.364	.318	.282	.245	.213	.175	.144
.2692	.415	.361	.320	.282	.244	.202	.167
.3028	.463	.407	.359	.316	.273	.278	.190
K	.796	.413	.144	.282	.223	.217	.106

Ave. K = .31 ± .17

Table 14. Spectra of dilute fluorene-concentrated tetranitromethane Fluorene, 1.71 x 10^{-3} moles/l.

	mmu						
c of TNM	410	420	430	440	450	460	470
.3310	.161	.111	.094	.080	.067	.056	.046
.4965	.224	.153	.128	.109	.091	.073	.058
.6620	.283	.191	.160	.137	.114	.091	.073
.8275	.337	.224	.188	.162	.135	.110	.090
1.159	.437	.283	.237	.203	.167	.135	.106
1.324	.482	.312	.260	.222	.185	.150	.118
K	.342	.465	.502	.479	.573	.632	.602

Ave. K = .51 ± .07

Table 15. Spectra of concentrated fluorene-dilute tetranitromethane Tetranitromethane, 0.008275 mole/l.

	mmu						
c of fluorene	410	420	430	440	450	460	470
.0673	.115	.098	.085	.074	.063	.052	.041
.1009	.166	.143	.125	.109	.094	.077	.063
.1346	.220	.190	.163	.145	.124	.102	.083
.1682	.267	.234	.203	.180	.152	.125	.104
.2019	.315	.276	.242	.213	.182	.151	.124
.2355	.364	.318	.282	.245	.213	.175	.144
.2692	.415	.361	.320	.282	.244	.202	.167
.3028	.463	.407	.359	.316	.273	.278	.190
K	.796	.413	.144	.282	.223	.217	.106

Ave. K = .31 ± .17

Table 16. Spectra of dilute fluoranthene-concentrated tetranitromethane Fluoranthene, 1.70 x 10^{-3} mole/l.

c of TNM mmu	410	420	430	440	450	460	470
0.1655	.169	.126	.104	.086	.070	.055	.042
.3310	.276	.207	.173	.144	.116	.092	.071
.4965	.370	.280	.230	.191	.155	.119	.092
.6620	.452	.339	.281	.233	.191	.149	.116
.8275	.530	.399	.331	.274	.221	.174	.135
.9330	.608	.446	.372	.310	.250	.196	.149
1.159	.662	.489	.411	.343	.278	.219	.169
1.324	.722	.516	.428	.353	.283	.223	.171
K	.671	.723	.783	.697	.800	.874	.835

Ave. K ≃ 0.77 ± .06

Table 17. Spectra of concentrated fluoranthene-dilute tetranitromethane Tetranitromethane, 8.28 x 10^{-3} moles/l.

c of fluoranthene mmu	440	450	460	470
.05936	.121	.096	.077	.060
.08904	.182	.144	.116	.093
.1187	.238	.190	.150	.118
.1484	.289	.231	.185	.145
.1781	.352	.282	.226	.177
.2078	.404	.322	.257	.203
.2374	.457	.369	.296	.235
.2671	.507	.411	.330	.262
K	.424	.269	.289	.144

Ave. K ≃ .28 ± .08

Table 18. Spectra of concentrated naphthalene-dilute picric acid in carbon tetrachloride

Picric acid, 4.05 x 10^{-4} mole/l.

c of naphthalene	mmu 400	405	410	415	420	425	430	435	440
.2188	.158	.148	.135	.122	.109	.103	.086	.074	.058
.3282	.199	.186	.167	.154	.140	.126	.104	.095	.077
.4376	.240	.224	.203	.184	.166	.149	.125	.111	.093
.5470	.258	.241	.218	.198	.180	.160	.133	.120	.098
.6564	.280	.269	.244	.219	.208	.181	.154	.129	.109
.7658	.309	.292	.266	.236	.210	.197	.166	.140	.117
K	2.08	1.86	1.96	2.56	3.09	1.81	1.82	2.34	1.97

Ave. K = 2.16 ± 0.33

Table 19. Spectra of concentrated naphthalene-dilute picric acid in ethylene dichloride

Picric acid, 4.10 x 10^{-4} mole/l.

c of naphthalene	mmu 400	405	410	415	420	425	430	435
.1570	.088	.076	.073	.069	.063	.063	.053	.041
.2324	.106	.100	.091	.084	.082	.072	.065	.054
.3139	.140	.132	.123	.112	.106	.095	.085	.070
.3924	.157	.146	.137	.126	.119	.103	.091	.078
.4709	.166	.157	.144	.137	.123	.107	.099	.081
.5494	.190	.176	.168	.155	.138	.121	.111	.089
.6278	.193	.184	.171	.161	.146	.131	.116	.095
K	2.30	1.80	1.74	1.70	2.07	2.44	2.10	2.03

Ave. K = 2.02 ± .21

Table 20. E for various molecular compounds

	420	430	440	450	460	470	480
Dilute acenaphthene[1]							
Concentrated acenaphthene					1444	1348	1243
Dilute fluoranthene	603	501	416	337	264	203	
Concentrated fluoranthene			881	705	564	446	
Dilute fluorene	442	369	317	264	212	169	
Concentrated fluorene			438	377	321		
Dilute naphthalene	2649	2349	1999	1664	1319	1008	726
Concentrated naphthalene	943	881	776	656	521	405	306
Dilute phenanthrene	695	597	530	463	403	350	
Concentrated phenanthrene		342	298	241	190	151	
Dilute chrysene		921	831	721	602		
Dilute anthracene							
Dilute 1,2-benzanthracene			692	621			
Dilute mesitylene				199	128	78	45
Concentrated naphthalene-dilute picric in CCl_4		631	459				
Concentrated naphthalene-dilute picric in CH_2ClCH_2Cl	633	503					

1. Tetranitromethane is the nitro component where no other is indicated.

Table 20 (continued)

	490	500	510	520	530	540	550	560
Dilute acenaphthene		952[2]	840	722	606	496	398	309
Concentrated acenaphthene	1139	1021	906	782				
Dilute naphthalene	498							
Concentrated naphthalene	226							
Dilute anthracene					437	398	359	320

	570	580	590	600
Dilute acenaphthene	235	175	127	92

[2] Limits of error are about one per cent.

Table 21. Spectra for ΔH of dilute naphthalene-concentrated tetranitromethane Naphthalene, 1.87 x 10^{-2} mole/l.; tetranitromethane, 0.3310, 1.324 moles/l.

T mmu	470		480		490		500	
28.2	.280	1.035	.208	.768	.142	.530	.095	.351
23.5	.287	1.085	.207	.790	.146	.552	.095	.361
21.3	.291	1.104	.212	.802	.147	.558	.098	.365
19.1	.295	1.097	.213	.799	.150	.564	.097	.369
16.3	.298	1.105	.216	.811	.150	.567	.100	.374
14.2	.301	1.115	.220	.823	.153	.576	.101	.377
ΔH	448		579	628	517			560

Ave. ΔH = -546 ± 51 cal.

Table 22. Spectra for ΔH of dilute anthracene-concentrated tetranitromethane Anthracene, 2.73 x 10^{-3} mole/l.; tetranitromethane, 0.8275, 1.159 moles/l.

T mmu	530		540		550		560	
27.1	.216	.268	.198	.244	.178	.220	.157	.194
21.2	.223	.275	.203	.251	.182	.226	.162	.201
17.5	.225	.278	.205	.255	.186	.230	.166	.204
13.4	.230	.283	.209	.259	.189	.234	.168	.207
ΔH	423	531	360	497	414	517		626

Ave. ΔH = -481 ± 70 cal.

Table 23. Spectra for ΔH of dilute phenanthrene-concentrated tetranitromethane Phenanthrene, 1.42 x 10^{-3} mole/l.; tetranitromethane, 0.9930, 1.324 moles/l.

	mmu							
T	440		450		460		470	
24.2	.240	.322	.200	.269	.166	.223	.133	.180
21.7	.241	.318	.201	.268	.164	.220	.135	.180
18.6	.244	.322	.205	.271	.168	.225	.136	.182
15.7	.247	.328	.206	.274	.171	.228	.137	.185
13.8	.248	.329	.208	.277	.171	.230	.139	.186
Δ H	362	704	438	743	392	846	480	514

Ave. ΔH = -560 ± 153 cal.

Table 24. Spectra for ΔH of dilute chrysene-concentrated tetranitromethane Chrysene, 3.93 x 10^{-4} mole/l.; tetranitromethane, 0.8275, 1.159 mole/l.

	mmu							
T	430		440		450		460	
27.3	.120	.150	.108	.137	.096	.120	.079	.100
21.8	.120	.150	.109	.138	.096	.122	.080	.101
18.9	.122	.151	.110	.138	.096	.122	.080	.101
14.4	.121	.152	.109	.139	.097	.123	.082	.103
Δ H	-320	-126	59	-172	-291	49	-212	-89

Ave. ΔH =+138 ± 111

Table 25. Spectra for ΔH of dilute 1,2-benzanthracene-concentrated tetranitromethane 1,2-benzanthracene, 3.09×10^{-4} mole/l.; tetranitromethane, 1.159, 1.324 moles/l.

mmu T	440		445		450		455	
22.1	.079	.088	.075	.083	.071	.078	.066	.074
19.3	.080	.089	.074	.084	.070	.078	.068	.078
14.5	.081	.089	.076	.086	.072	.081	.068	.078

Ave. $\Delta H \cong 0$

Table 26. Spectra for ΔH of dilute mesitylene-concentrated tetranitromethane Mesitylene, 1.44×10^{-2} mole/l.; tetranitromethane, 0.9930, 1.324 moles/l.

T	450		460		470		480	
27.6	.376	.484	.242	.311	.143	.187	.081	.106
21.5	.391	.502	.246	.319	.147	.191	.082	.109
17.7	.401	.515	.256	.331	.152	.197	.086	.113
14.3	.407	.523	.259	.336	.156	.199	.087	.113
ΔH	798	754	753	843	1104	500	935	

Ave. $\Delta H \cong -812 \pm 127$

Table 27. Spectra for Δ H of dilute acenaphthene-concentrated tetranitromethane Acenaphthene, 1.58 x 10^{-2} mole/l.; tetranitromethane, .3310, 1.159 moles/l.

mmu T	540		560		580		600	
24.4	.224	.728	.139	.454	.079	.260	.037	.134
22.7	.219	.722	.140	.457	.079	.263	.041	.137
20.5	.226	.741	.139	.459	.081	.267	.041	.137
18.6	.233	.756	.136	.456	.082	.270	.040	.138
16.4	.234	.760	.146	.475	.085	.277	.038	.138
14.5	.238	.774	.149	.481	.085	.281	.042	.144
Δ H	923	725	1089	837	828	1032	/	1148

Ave. Δ H = -940 ± 128 cal.

Table 28. Spectra for ΔH of dilute fluorene-concentrated tetranitromethane Fluorene, 1.71 x 10^{-3} mole/l.; tetranitromethane, 0.9930, 1.324 moles/l.

mmu T	440		450		460		470	
27.1	.186	.243	.159	.207	.134	.173	.106	.139
25.2	.187	.246	.161	.211	.134	.176	.108	.141
22.0	.190	.248	.164	.212	.136	.175	.109	.140
18.7	.193	.254	.166	.215	.137	.179	.112	.144
15.8	.197	.257	.169	.219	.141	.182	.114	.148
13.3	.198	.258	.171	.221	.143	.184	.116	.149
Δ H	729	886	871	777	1028	900	1143	1072

Ave. ΔH = -926 ± 117

Table 29. Spectra for ΔH of dilute fluoranthene-concentrated tetranitromethane Fluoranthene concentration 1.70 x 10^{-3} mole/l.; tetranitromethane concentration 0.8275, 1.324 moles/l.

T mmu	440		450		460		470	
26.3	.287	.428	.240	.355	.194	.287	.152	.227
23.7	.288	.431	.240	.357	.194	.288	.153	.228
21.0	.294	.439	.244	.363	.197	.294	.155	.231
18.9	.295	.442	.247	.369	.199	.298	.156	.233
16.5	.297	.445	.247	.371	.200	.300	.157	.235
13.8	.299	.448	.249	.373	.202	.303	.158	.237
ΔH	532	572	369	1097	566	1130	532	929

Ave. ΔH = -716 ± 252 cal.

Table 30. Spectra for ΔH of concentrated naphthalene-dilute picric acid in carbon tetrachloride Picric acid, 4.35 x 10^{-4} mole/l.; naphthalene, 0.5500, 0.8800 mole/l.

T mmu	425		430		435		440	
25.1	.192	.248	.166	.217	.143	.188	.121	.160
23.0	.197	.248	.173	.219	.149	.190	.127	.164
16.6	.212	.261	.185	.230	.158	.197	.133	.169
12.8	.226	.274	.195	.235	.168	.206	.142	.176
7.7	.243	.294	.212	.258	.182	.224	.153	.191
ΔH	5720		5980	5720	5460	7260	5430	

Ave. ΔH = -5930 ± 460 cal.

Table 31. Spectra for ΔH of concentrated naphthalene-dilute picric acid in ethylene dichloride

Picric acid, 4.10×10^{-4} mole/l.; naphthalene, 0.3924, 0.5494 mole/l.

mmu T	415		420		425		430	
22.4	.108	.137	.099	.125	.087	.111	.072	.092
19.9	.110	.146	.097	.130	.088	.117	.077	.103
16.6	.112	.151	.102	.136	.091	.124	.079	.106
13.6	.120	.158	.106	.141	.097	.127	.083	.110
9.4	.130	.167	.120	.162	.106	.135	.092	.118
6.2	.137	.173	.125	.152	.111	.140	.099	.123
ΔH	3830	4290	4140	3540	4020	4340	4640	4770

Ave. $\Delta H = -4200 \pm 330$

Table 32. Summary of the thermodynamics of the formation of molecular compounds from the components

	K(2)	ΔF°	ΔH°	ΔS°
Dilute naphthalene[1]	0.095	1395	-546	-6.52 e.u.
Concentrated naphthalene	.13			
Dilute anthracene	.28	750	-481	-4.13
Dilute phenanthrene	.61	291	-560	-2.85
Concentrated phenanthrene	.72			
Dilute chrysene	.62	282	138	-0.48
Dilute 1,2-benzanthracene	uncertain		very small	
Dilute benzene	small			
Dilute mesitylene	.16	1083	-812	-6.36
Dilute acenaphthene	.097	1383	-940	-7.81
Concentrated acenaphthene	.092			
Dilute fluorene	.51	398	-926	-4.45
Concentrated fluorene	.31			
Dilute fluoranthene	.77	154	-716	-2.92
Concentrated fluoranthene	.28			
Concentrated naphthalene-dilute picric in CCl_4	2.16	-456	-5930	-18.40
Concentrated naphthalene-dilute picric in CH_2ClCH_2Cl	2.02	-417	-4200	-12.70

1. Tetranitromethane is the nitro compound and carbon tetrachloride is the solvent where no other is named.

2. All quantities are at 25° C.

Table 33. Ultraviolet and visible absorption spectra of some molecular compounds and their components

compound mmu	TNM[1]	Picric[2]	Benzene[3]	Naphth.[4]	Benzene-TNM[5] Obs.	 Calc.
250	.880	.715	.046	.120	.518	.463
260	.652	.457	.028	.222	.367	.340
270	.500	.257	0	.279	.257	.250
280	.379	.191	0	.228	.191	.190
290	.272	.193	0	.107	.140	.136
300	.189	.232	0	.015	.101	.095
310	.123	.313	0	0	.075	.062
320	.090	.439	0	0	.063	.045
330	.066	.618	0	0	.063	.033
340	.067	.820	0	0	.077	.033
350	.065	.970	0	0	.086	.032
360	.054	1.011	0	0	.072	.027
370		.945	0	0		
380		.840	0	0		

1. 8.28×10^{-4} M. tetranitromethane.
2. 8.52×10^{-3} M. picric acid.
3. 1.12×10^{-4} M. benzene.
4. 1.32×10^{-3} M. naphthalene.
5. This and succeeding mixtures are mixtures of equal volumes of the solutions of the components given in columns 2-5. The calculated values are determined by assuming the density is the average of those of the two solutions.

Table 33 (continued)

compound	Benzene-picric		Naphthalene-TNM		Naphthalene-picric	
mmu	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
250	.387	.380	.503	.500	.425	.418
260	.234	.242	.448	.437	.337	.339
270	.128	.127	.402	.389	.265	.268
280	.091	.095	.312	.303	.203	.210
290	.092	.096	.198	.190	.145	.150
300	.118	.116	.115	.102	.125	.123
310	.167	.156	.076	.065	.170	.156
320	.238	.219	.057	.043	.239	.219
330	.337	.309	.045	.033	.338	.309
340	.442	.410	.048	.033	.443	.410
350	.522	.485	.048	.032	.528	.485
360	.540	.505	.041	.027	.549	.505
370	.502	.472			.508	.472
380	.444	.420			.452	.420

Table 34. Continuous variations for naphthalene-tetranitromethane, 0.0823 mole/l.

mmu

c of TNM	420	430	440	450	460	470	480
.0082	.098	.083	.072	.063	.052	.040	.029
.0164	.152	.132	.112	.098	.079	.061	.045
.0246	.185	.161	.139	.119	.096	.072	.052
.0328	.225	.197	.168	.141	.113	.086	.062
.0411	.236	.204	.174	.145	.116	.089	.065
.0492	.217	.188	.162	.134	.109	.084	.060
.0574	.208	.178	.147	.129	.102	.082	.061
.0656	.158	.136	.111	.098	.077	.062	.048
.0738	.092	.077	.062	.057	.044	.037	.028

Table 35. Continuous variations for acenaphthene-tetranitromethane, 0.0823 mole/l.

mmu

c of TNM	430	440	450	460	470	480	490	500	510	520
.0082	.109	.101	.095	.088	.078	.075	.067	.062	.053	.047
.0164	.173	.164	.153	.145	.132	.124	.111	.099	.088	.078
.0246	.221	.207	.198	.188	.171	.159	.145	.132	.117	.101
.0328	.259	.245	.233	.217	.202	.187	.172	.153	.133	.114
.0411	.262	.248	.236	.219	.206	.191	.175	.155	.134	.116
.0492	.247	.234	.222	.207	.196	.181	.166	.147	.128	.111
.0574	.224	.208	.198	.188	.173	.160	.148	.128	.114	.096
.0656	.164	.154	.146	.139	.128	.118	.110	.095	.084	.071
.0738	.089	.080	.078	.074	.067	.062	.059	.049	.044	.036

Table 36. Continuous variations for mesitylene-tetranitromethane, 0.4110 M

mmu					
c of TNM	450	460	470	480	490
0.0411	.447	.288	.167	.096	.053
.0822	.787	.507	.297	.168	.092
.1233	1.020	.654	.387	.218	.118
.1644	1.161	.755	.443	.253	.137
.2055	1.200	.775	.458	.258	.140
.2466	1.148	.743	.435	.246	.132
.2877	1.015	.643	.387	.219	.116
.3288	.758	.482	.238	.163	.087
.3699	.440	.282	.169	.096	.051

Table 37. Continuous variations for benzene-tetranitromethane, 8.270 M.

mmu					
c of TNM	440	445	450	455	460
0.827	.747	.448	.259	.151	.084
1.654	1.150	.694	.404	.233	.129
2.481	1.340	.800	.467	.268	.148
3.308	1.369	.825	.473	.274	.155
4.135	1.292	.763	.435	.249	.141
4.962	1.109	.644	.364	.207	.117
5.789	.868	.504	.288	.162	.091
6.616	.558	.320	.180	.101	.056

IV. CONCLUSIONS

A. Proof and significance of a true equilibrium.

Whether or not there is a true equilibrium in solution is an important question in the field of molecular compounds. It is believed that this question is not answered satisfactorily in the literature. If there is a chemical reaction, it should be possible to show there is a true equilibrium; if there is a polarization of the kind that Gibson and Loeffler postulate, then a true equilibrium would not be observed. Those who postulate a polarization are either vague or noncommittal on this point. If there is a true equilibrium, then either one of the chemical reaction theories or some modification of a polarization theory which includes the idea of an equilibrium must be the correct theory which explains the phenomena observed for molecular compounds. It is shown elsewhere that the chemical reaction theories (an ionic or a covalent bond form) are improbable. The experimental evidence offered in this paper shows there is a true equilibrium. Thus, strong--but not conclusive--evidence for the existence of the polarization aggregate discussed earlier is given.

That there is true equilibrium is deduced from the fact that the curve obtained from plotting c/d against c is linear, as supposed; the equilibrium constants determined at wide extremes of concentration are the same, within rather large limits of error; the extinction coefficients at extremes of concentration are close enough to indicate they are probably of the same compound.

Although the equilibrium constants determined at extremes of concentration are sometimes not close (e.g. 0.77 and 0.28 for dilute and concentrated fluoranthene, respectively) the limits of error can be seen to be so large that no conflict with the existence of a true equilibrium can be deduced. It is believed that the cases in which there is good agreement (naphthalene, acenaphthene, phenanthrene) are not accidental. It is particularly significant that calculation of the extinction coefficients at these extremes of concentrations shows the best agreement where there is the best agreement between the two equilibrium constants (acenaphthene-tetranitromethane). In Table 20 it is seen that the E values for this molecular compound agree to within five per cent at the three wavelengths for which measurements were made at both extremes of concentration; this is true in spite of the fact that E is very sensitive to the value of K used (The two K values differ by about this amount.), and in spite of the fact that E values at the extremes are theoretically not exactly the same (this is discussed below). The difference between the extinction coefficients calculated at each extreme can be seen to be appreciable where the equilibrium constants become farther apart, as would be expected. It is true, however, that this difference always is in the direction it would be expected to be from a consideration of the equilibrium constants.

B. The factors affecting results

There are four principal reasons for the error observed: 1. The equilibrium constants are small; the calculations described earlier are such that large equilibrium constants could be determined much more accurately. 2. The error in the optical measurements is high compared to other physical measurements, and this introduces a large error in small equilibrium constants. 3. In some cases, as with 1,2-benzanthracene, the solubility is very low and only a small amount of color is produced. There is a large error in measuring low optical densities with the Beckman instrument. For this reason no constant could be calculated for 1,2-benzanthracene-tetranitromethane. 4. There is a slight change of solvent in going from, for example, a tetranitromethane concentration of 0.1655 M - 1.490 M, as recorded in Table 12 for concentrated tetranitromethane-dilute acenaphthene. This could introduce an error, since absorption spectra change with a change of solvent.

It is not possible to calculate equilibrium constants with concentrated benzene and concentrated mesitylene solutions, but this is not due to experimental error or to the lack of a true equilibrium. Examination of the data given in Tables 9 and 11 shows that the concentration ranges are 1.12 M - 8.96 M and 0.718 M - 6.46 M for benzene and mesitylene, respectively. These represent concentrations much higher than those of other solutions, and in the benzene and mesitylene solutions there is again actually a change of solvent; the most dilute of these solutions contains almost ten percent hydrocarbon. In such solutions the activities of the components are altered, and the absorption spectrum changes due to a change of solvent.

It is difficult to determine the equilibrium constant in the dilute benzene-concentrated tetranitromethane solution because the nitro compound is very concentrated (1.324 M - 3.972 M) and because the constant is very small. That the constant is small is evident from the data and from the conclusions of other workers (Hammick, Briegleb, and coworkers).

It might be expected that the ratio of the extinction coefficients calculated at the two extremes of concentration would at least be constant at different wavelengths, even if the extinction coefficients calculated at the two extremes are not the same. This is not true for two reasons: 1. E is only approximately, but not exactly, proportional to 1/K. 2. There is at least a small change of solvent in going from one extreme to the other; in concentrated tetranitromethane solutions there is always at least five per cent tetranitromethane. The ratio of the extinction coefficients is therefore not constant for different wavelengths where the two equilibrium constants are not very close to each other. If, however, optical densities are compared for solutions at extremes of concentration, then the first of these objections does not hold. Since the other objection does hold, actual calculations reveal that the ratio is not perfectly constant with a change is wavelength, in contrast to the constant ratio obtained between optical densities of two different solutions which have nearly the same concentrations of components.

The values obtained for the heat of reaction are only approximate because of some of the same reasons cited for K and E value inaccuracies; it is also true that the temperature coefficient of color is small and the extinction coefficient, which is not accurately known, must be used for the calculation. No calculations could be made in the case of benzene-tetranitromethane because the density as a function of temperature of these mixtures was not determined.

The data of the method of continuous variations confirm some of the results obtained from the determination of equilibrium constants. The components of the molecular compounds of tetranitromethane with naphthalene, acenaphthene, and mesitylene are seen to be in a ratio of 1:1 from Figs. 3 and 4; Fig. 5 shows benzene-tetranitromethane to give results from which no conclusion can be made; neither a 1:1 nor a 1:2 complex is indicated. It would be expected that benzene-tetranitromethane would behave in an irregular manner because of the change in solvent which occurs here.

Careful examination of Figs. 3 and 4 reveals the curves to be slightly asymmetric, even though 1:1 compounds are indicated. Experimental error will cause the peak to be moved slightly, and this is in accordance with the conclusions made by Kingery and Hume (87).

C. The stability of molecular compounds. Some generalizations concerning stability can be made from the data given in this paper. 1. The stability of all tetranitromethane molecular compounds, whether measured by the equilibrium constant or by the heat of reaction, is much less than the stability of the corresponding compounds formed by picric acid and (according to Briegleb and others) s-trinitrobenzene. This is in accordance with the view of Briegleb (discussed earlier) that aromatic nitro compounds form molecular compounds which are more stable than those of aliphatic nitro compounds.

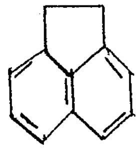
2. The molecular compounds of both tetranitromethane and of picric acid are weak. This is shown not

only by the small equilibrium constants and the small heats of reaction, but also by the nature of the ultraviolet absorption spectra of four of these compounds given in Table 33. It is seen that the presence of a molecular compound does not alter the ultraviolet spectra. For a noticeable difference in the ultraviolet spectra the molecular compound would have to be present in fairly large concentration, and its spectrum would also have to be appreciably different. Molecular compounds do not meet these conditions.

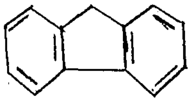
3. The relative stability of molecular compounds of tetranitromethane can be determined from the equilibrium constants, but because the limits of error are wide, the heats of reaction cannot be used for such a comparison. As Briegleb and others indicate, increasing aromaticity increases molecular compound stability. This seems to be true if the equilibrium constants of compounds of benzene, naphthalene, anthracene, chrysene, and phenanthrene are considered; the constants increase in the order given. The methyl groups of mesitylene tend to donate electrons to the ring, and they therefore make the ring more aromatic (better electron donor); accordingly the equilibrium constant for the formation of the mesitylene compound is much higher than that of the benzene compound. Hexamethylbenzene should form an even stronger complex than mesitylene. Although the equilibrium constant

could not be measured, it is of interest to note that hexamethylbenzene-tetranitromethane solutions were observed to have a very deep red color. The deep red color probably indicated a strong interaction (in comparison with the yellow color of the benzene and mesitylene mixtures), but this is by no means certain.

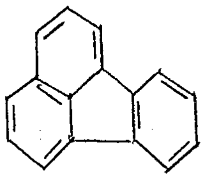
Acenaphthene, fluorene, and fluoranthene have the structures indicated.



Acenaphthene



Fluorene



Fluoranthene

It might be expected that acenaphthene, a derivative of naphthalene which is partly aliphatic, would form molecular compounds of greater stability than naphthalene. Their equilibrium constants are very close, however, and this expectation is not realized. Fluorene and fluoranthene appear to be much better electron donors in molecular compound formation than acenaphthene.

4. In the one example given (naphthalene-picric acid) it seems apparent that carbon tetrachloride is a slightly better solvent for stability than is ethylene dichloride. Both are inert solvents, but the dielectric constant of ethylene dichloride is five times that of carbon tetrachloride. This may indicate that a smaller interaction energy is necessary for formation of the molecular compound in the solvent of higher dielectric constant, as is expected.

5. In the calculation of the heat of reaction, the correction for the change of the volume of the solvent with temperature was made. Thus, the heats of reaction obtained are for the condition of constant volume. All but one of the heats determined has a negative value, indicating a negative color coefficient of temperature at constant volume and showing, as pointed out earlier, that at least part of the polarization theory of Gibson and Loeffler is incorrect.

6. All the entropies of formation of molecular compounds are negative. This indicates that there is an orientation effect in the formation of a molecular compound. If there are ions formed from the intermediate polar molecule, it would be difficult to predict the sign of ΔS.

V. SUMMARY

A. The formation of molecular compounds of tetranitromethane with aromatic hydrocarbons has been studied at different temperatures by a spectrophotometric method.

B. Equilibrium constants and free energies of formation have been calculated from the data.

C. Heats and entropies of formation of the compounds have been calculated.

D. The stabilities of the compounds have been correlated with the nature of the constituent molecules.

E. The various theories concerning the nature of the interaction between the components of a molecular compound have been discussed in the light of the data obtained in the present and in the earlier work, and a modification of a polarization theory has been suggested to represent the true nature of the interaction.

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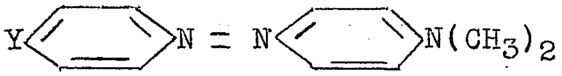
Part II. The Ionization Constants of Some Para-substituted p'-Dimethylaminoazobenzenes.

I. INTRODUCTION

For many years the structure of dyes and of the ions they form in solution has been a subject of much discussion in the literature. These structures are discussed in connection with dye color. It might be expected that the only valid conclusions would be those made since the inception of modern ideas concerning resonance and molecular structure, but some ideas advanced earlier are helpful in understanding the present problem.

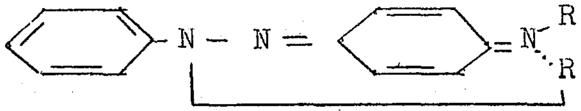
The dyes to be discussed in this paper are azo dyes of the type

I.



where Y may be Cl, I, H, CH_3, $C(CH_3)_3$, SCN, SeCN, OCH_3, or NO_2. The parent substance, where Y H, is well known, and its structure is discussed by several workers including Prideaux who in 1917 (1) postulated the following structure for the free base:

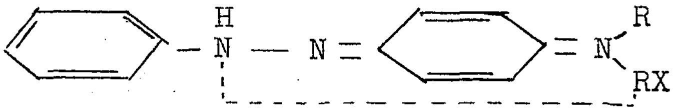
II.



The dots (....) indicate "subsidiary" valence while the unbroken lines indicate "primary" valence. R is an alkyl group. The free base is yellow. In the presence of an acid, HX, the proton adds to the azo nitrogen farthest from the amino group, and the "primary" valence between R and the azo nitrogen is broken. According to the theory of Prideaux, X adds to this same R group, and now this R group is connected to the amino nitrogen with a primary valence. Acid solutions of (I) are red.

According to Hantzch and Burawoy (1930) the structure of the "salt" form should be slightly different (2):

III.



This they conclude from an examination of the spectra of the base in alcohol, in dilute acid, and in concentrated sulfuric acid. The ideas of Hantzch became the subject of dispute. However, it is not necessary to give more than a representation of the early ideas on the subject here.

The ideas the early workers had on the origin of the color of these dyes were rather vague and uncertain. Prideaux (ibid., p. 82) refers to light absorption as being due to the vibration of atoms or valency lines of force; this is seen to be related to modern ideas on molecular spectroscopy if the infrared spectrum is included in the term "light absorption". He says it seems that at least some great changes of color are due "...to very fine adjustments of vibrations within the molecule..." Baly (3) suggests that the self-neutralized affinities on the molecule may be opened up by light or the residual affinity of the solvent. He says an increase in the residual affinity of the solvent displaces the absorption band toward the red. In this connection it must be noted that the work of Purvis (4) shows that in high dilution some substances absorb about the same as their vapors. Baly later elaborated on this theory (5).

While our modern ideas on the nature of the chemical bond are much clearer and more useful than the ideas expressed in II. and III. above, our modern ideas on the origin of the color of these molecules are not clear, well-defined, and universally accepted.

Lewis and Calvin (6) in a review article on the color of organic molecules suggest that a separation of charge in a molecule makes possible a low energy electronic transition; this corresponds to absorption of light of longer wavelength than would be absorbed if there were no separation of charge. With molecules that absorb strongly in all or nearly all of the ultraviolet region, as do these dyes, absorption of the free base and of the ions formed in acid solution is moved into the visible region. The same idea is used by Pauling (7) to explain the yellow color of the picric acid molecule and the color of the other molecules.

There are a large number of other effects discussed in modern spectroscopic literature; it is not the purpose of this paper to discuss at length the spectroscopy of these dyes. The purpose of this paper is to use the color of the nine dyes which have the general formula (I) and their ions in acid solutions as a means of analysis in calculating ionization constants. It is intended that these constants should make it possible to determine the relative importance of various resonance contributions to the dye molecule by comparing the effect of different substituents. The effect of these substituents on the basicity of the dyes is discussed.

These nine dyes are all weak bases which can take on two protons. The number of protons which add on, and the nitrogen atoms to which they add, are other results of this investigation. It is stated in the literature (8) that the parent dye of this group, p-dimethylaminoazobenzene takes on two protons, but quantitative evidence is not given. The first proton adds to the free base in acid solutions dilute enough so that the pH is measurable by ordinary means. The second proton adds to the singly protonated base in strong acid solutions which may be between 10% and 80% sulfuric acid. These facts are easily observed by the marked color changes which accompany the first and the second addition of a proton.

The ionization constant corresponding to

$$\text{(A)} \qquad HB^+ \longrightarrow H^+ + B$$

where B is the free base, can be measured by methods by which the ionization constants of ordinary acid-base indicators are measured. It can be easily shown that,

$$(1) \qquad pK_1 = pH - \log \frac{(B)}{(BH^+)} - \log \frac{f_B}{f_{BH^+}}$$

which is a form of the Henderson-Hasselbach equation, where K_1 is the ionization constant for (1) and where (B) and(BH^+) represent concentrations and f_B and f_{BH^+} represent activities; for the corresponding ionization of the doubly protonated ion K_2 is used.

Since both the free base and the ion have characteristic absorption bands, it should be possible to use Beer's law to evaluate pK_1 in solutions of known pH by the use of (1). It would be possible to calculate (B) and (BH^+) directly if the free base and the ion absorbed in mutually exclusive regions. Since there is no wave length at which one of the two species (free base and first ion) does not absorb while the other does absorb, certain modifications must be made (9).

The combined Beer-Lambert law,

$$(2) \qquad E = \frac{-\log I/I_o}{cl}$$

where E is the absolute extinction coefficient, $-\log I/I_o$ is the optical density, c is the concentration of the colored substance, and l is the length of the light path, may be written as

$$(3) \quad -\log I/I_o = (E_B c_B - E_{BH^+} c_{BH^+})l$$

where E_B and E_{BH^+} are the absolute extinction coefficients for the free base and the first ion, respectively, and c_B and c_{BH^+} represent the molar concentrations of these substances. The substitution of the terms in parentheses in (3) for the product E_c in (2) is seen to be justified when it is remembered that a measure of the color observed is $E_B + E_{BH^+}$ if the solution is 1 M with respect to both species; c_B and c_{BH^+} are weighting factors. (2) may also be written as

$$(4) \quad -\log I/I_o = E(c_B + c_{BH^+})l$$

Equating the right hand sides of (3) and (4),

$$(5) \quad Ec_B + Ec_{BH^+} = E_B c_B + E_{BH^+} c_{BH^+}$$

Rearranging, it may be seen that

$$(6) \quad \frac{c_B}{c_{BH^+}} = \frac{E - E_{BH^+}}{E_B - E}$$

Equation (1) becomes

$$(7) \quad pK_1 = pH - \log \frac{E - E_{BH^+}}{E_B - E} \quad -\log \frac{f_B}{f_{BH^+}}$$

E is the "apparent extinction coefficient" calculated from observed optical densities at known total concentration of $c_B + c_{BH^+}$; E_{BH^+} and E_B represent the same quantity calculated when the first ion and the free base, respectively, are present alone. The use of this equation in the present work is explained later.

The determination of the ionization constant for the reaction

(B) $BH_2^{++} \longrightarrow BH^+ + H^+$

can be calculated only if the hydrogen ion activity is known and if suitable spectrophotometric measurements can be made. For each of these conditions a modification of the above method must be made.

The second proton adds to the singly protonated dye molecule only in strong acid solutions, and here there is no way to measure hydrogen ion activity. Hammett and Deyrup (8) report a function which is a measure of the acidity of strong acid solutions; it cannot, however, be said to be the hydrogen ion activity. They measure the tendency of a strong acid to protonate a weak, uncharged base, and for several acids they report H_o, a measure of the tendency of a strong acid to protonate an uncharged base. H_+ is an analogous function, and it is a measure of the tendency of a strong acid to protonate a base which has a single positive charge. It is this latter function which should be used in the present work, but the values of H_+ have never been determined. The results obtained in this work show that H_o and H_+ are not the same. It is not necessary, as will be seen, to know H_+ at various acidities to <u>compare</u> the various dyes. H_o can be used for this comparison. This is discussed more fully later.

Hammett and Deyrup determine H_o by making spectrophotometric measurements on strong acid solutions of bases which can take on only one proton. For such a solution pK, where K is the ionization constant, is given by

$$(8)\quad pK = -\log \frac{a_{H^+}a_B}{a_{BH^+}} = -\log \frac{c_{H^+}c_B}{c_{BH^+}} - \log \frac{f_{H^+}f_B}{f_{BH^+}}$$

where c is the concentration and f is the activity coefficient. The activity coefficient term drops out in dilute aqueous solutions, since concentrations and activities are identical in such solutions. They determine pK from (8) for a base which adds a proton in dilute aqueous acid. It is true that if two bases, B and C, are compared in any solution

$$(9)\quad pK_B - pK_C = -\log \frac{c_B c_{CH^+}}{c_{BH^+}c_C} - \log \frac{f_B f_{CH^+}}{f_{BH^+}f_C}$$

They assume throughout this work that

$$(10)\quad \frac{f_B}{f_{BH^+}} = \frac{f_C}{f_{CH^+}}$$

for any two weak bases. Then $pK_B - pK_C$ may be determined if $\frac{c_B}{c_{BH^+}}$ and $\frac{c_{CH^+}}{c_C}$ are known, since the last term of the equation drops out. These may be known from spectrophotometric data, as pointed out above. If pK_B is known (for substance B (8) may be used) then pK_C may be known even if the measurements for the use of (9) are made in a solution in which the pH is not measurable. (9) may then be used in comparing bases C and D, even though D is a weaker base than C; in this manner the pK value of a very weak base, which adds a proton only in 90-95 per cent sulfuric acid, may be known if several bases of intermediate strength such as are described above are used in a series of comparisons. It must be remembered that pK values obtained in this way are referred to a dilute aqueous solution as a reference standard.

We may rewrite (8) for any weak base:

$$pK = -\log \frac{a_B}{a_{BH^+}} - \log a_{H^+}$$

This is rewritten so that

$$(11) \quad pK = -\log \frac{c_B}{c_{BH^+}} + H_o$$

which defines the acidity function, H_o. It is seen that H_o is not the pH, since H_o also takes into account the substitution of concentration for activities. However, if (10) is valid, then H_o is independent of the weak base used. H_o may now be known for any acid solution in which a weak base whose pK is known takes on a proton.

Once H_o is known for acid of a given strength, the pK of a weak base which adds a proton in acid of that strength may be calculated. This is done in the present work; details concerning this are discussed later.

It was mentioned earlier that pK's of very weak bases could only be measured if suitable spectrophotometric measurements can be made. It is true that both the first and the second ion have characteristic colors in all the dyes studied here, but a difficulty arises in evaluating the log $\frac{E - E_{BH^+}}{E_B - E}$ term. E_B, E, and E_{BH^+} must be calculated from solutions which must of necessity be very different in acid strength. This means that there is essentially a change of solvent, and the absorption of a given species changes with a change in solvent. The log term mentioned above cannot be evaluated correctly unless the three extinction coefficients are calculated from the same medium. Flexser, Hammett, and Dingwall (9) discuss two methods, the least squares and the isobestic point, by which this difficulty may be eliminated; they show from experiment that the two methods give the same results. In this work the isobestic point method is used exclusively.

If the absolute extinction coefficients of two species in equilibrium are identical at some wavelength, then all possible mixtures of these two species should also have the same apparent extinction coefficient (10) at this wavelength. The absorption curves of all mixtures should intersect at a point if there is no medium effect; this point is called the isobestic point. In the determination of the first ionization constant of the dyes in this work it was noted that there is such an isobestic point; there is therefore no medium effect in these solutions. But in the determination of the second ionization constant (for reaction (B)) it is seen that, although all absorption curves obviously should intersect at a point, they do not do so. Hammett and coworkers assume that there would be a true isobestic point if there were no medium effect, and they correct for the medium effect by using this assumption. They shift all absorption curves laterally so that they all do intersect at one point. The curves are shifted so that two which apparently are close to the middle of the ionization region are not moved. The use of this procedure assumes that the medium effect is one in which there is only a lateral shift in the absorption curve, not one in which the height or shape is altered. Since this treatment gives good agreement with the least squares method of correcting for the medium effect in the determination of the pK for acetophenone, and the pK's calculated vary with wavelength only in a random way, Hammett and coworkers conclude that this assumption is a valid one.

FIG. 1 pK$_1$ for Y=CH$_3$

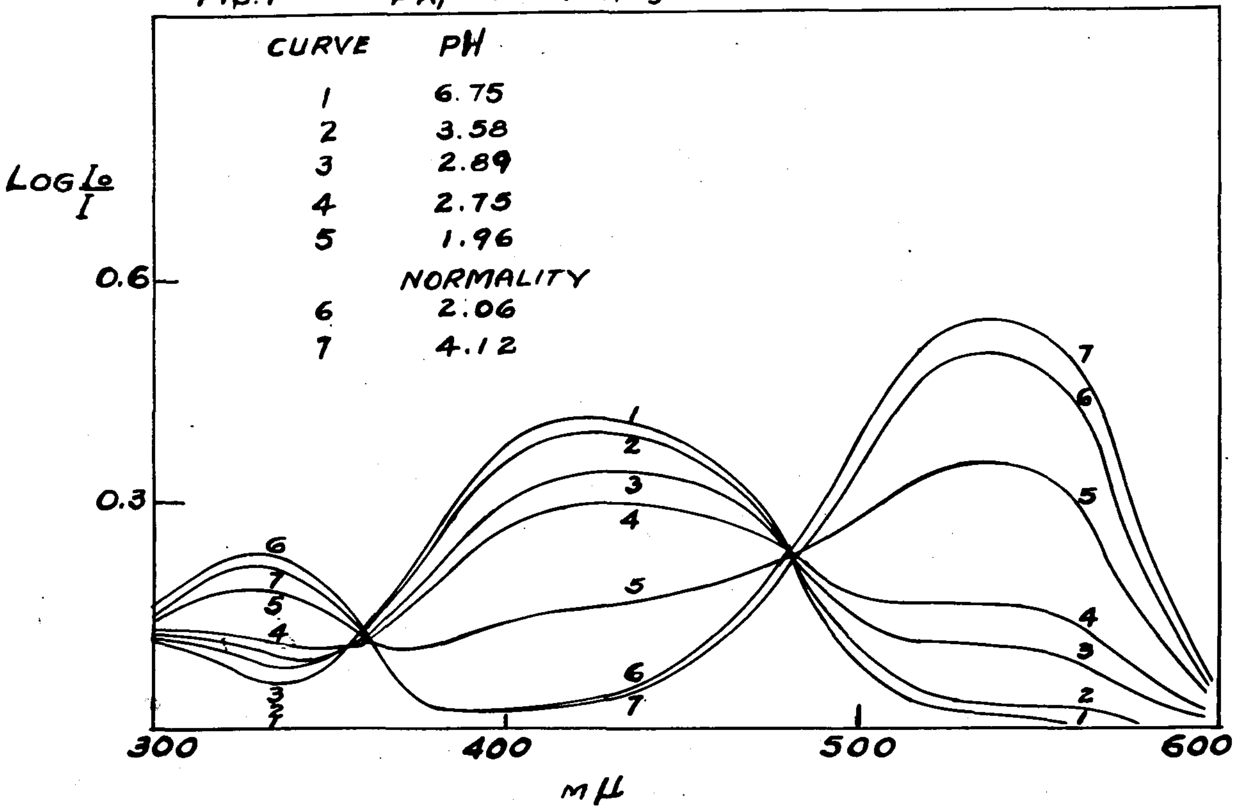
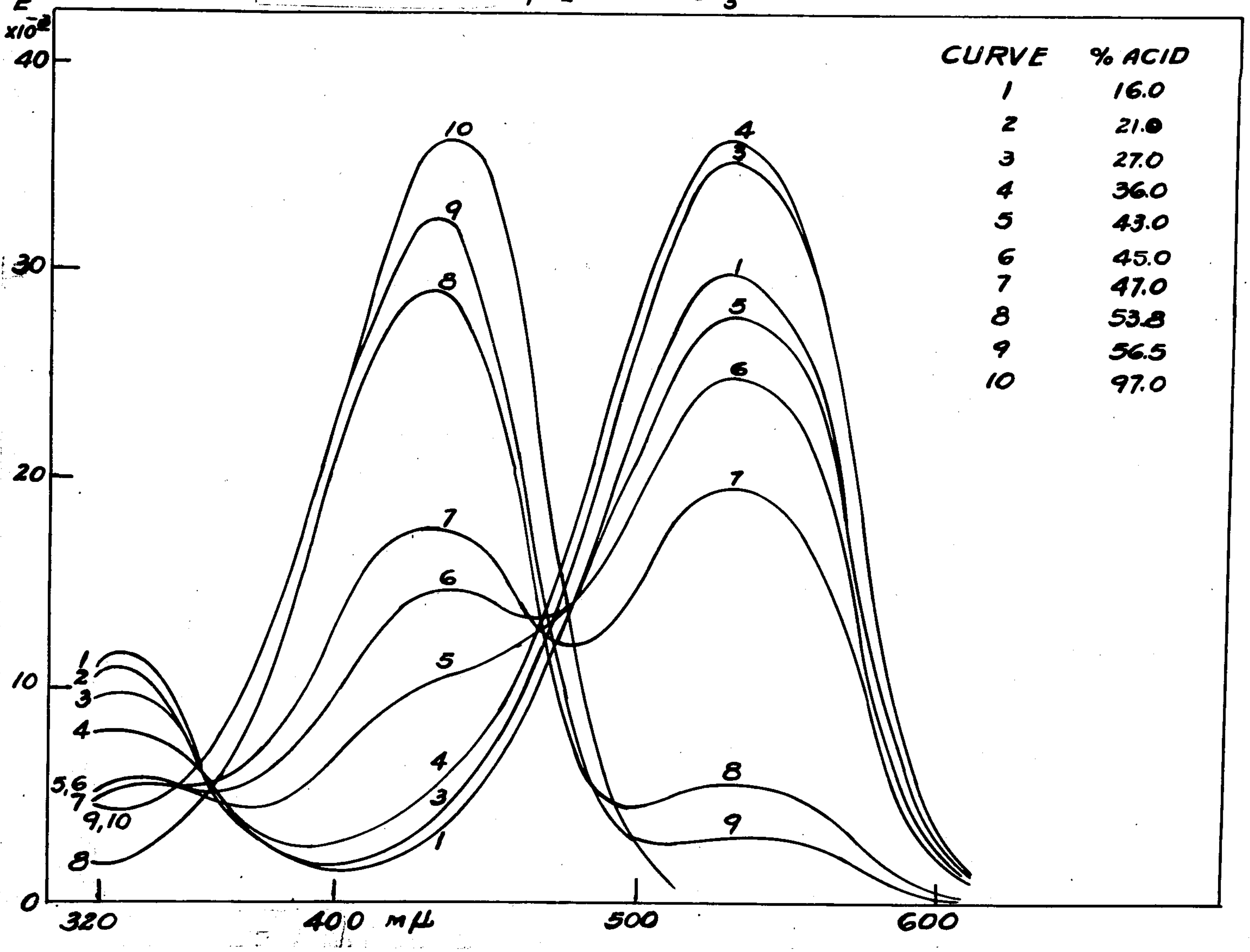


FIG. 2

pK_2 FOR $Y = CH_3$



II. EXPERIMENTAL

A. Materials. The preparation and characterization of these dyes are described elsewhere (11).

Sulfuric acid was Baker's c.p. grade; it was analyzed by standardization against 0.25 N sodium hydroxide, which was standardized against potassium acid phthalate, Baker's c.p. grade.

B. Procedure. The spectra of the nine dyes were measured in sulfuric acid solutions, ranging from pH = 6.75 to 96.00% sulfuric acid, on the Beckman Quartz Model DU spectrophotometer. (Two compounds, where Y = SCN and SeCN, decomposed in strong acid solution, and no second ionization constant could be determined.) Approximately 1.0 centimeter Corex (glass) cells were used, and spectra were recorded from 300-600 m mu. Fig. 1 gives a typical series of absorption curves of solutions of different strengths of sulfuric acid. Since it was necessary to use 50% ethanol and 50% sulfuric acid-water in dilute solutions to keep the dye in solution, only an apparent pH could be measured on the Beckman glass electrode pH meter.

The optical densities (x 10^3) and pK_1 values calculated are given in Tables 1-9; the apparent extinction coefficients, which are d/c, where d is the optical density and c is the concentration in moles per liter, and pK_2 values, are given in Tables 10-16. The dye concentration used in both dilute and strong acid was of the order of 10^{-3}-10^{-6} molar, but measurements in dilute acid were made on solutions of the same dye concentration for any one dye; thus $\log \frac{E-E_{BH^+}}{E_B-E} = \log \frac{d-d_{BH^+}}{d_B-d}$. The optical densities given are therefore on an arbitrary scale.

In order to use (7) to calculate pK_1 it would be necessary to know the activity coefficients of the free base and its first ion. It is assumed that in solutions as dilute as these the error introduced by substituting concentrations for activities is much less than the experimental error. The activity coefficient term is therefore omitted because it approaches zero as the activity coefficients approach unity.

For some of the dyes it was necessary to use 4.115 N. sulfuric acid in order to obtain the spectrum of BH^+. In those cases it was noted that there is a medium effect, and it became necessary to shift the absorption curve of this solution in order that it might pass through the isobestic point.

For both pK_1 and pK_2 calculations it is necessary to have the spectrum of BH^+ when this ion is not in the presence of the free base or the second ion. This was actually rather difficult to obtain, since there is only a very narrow range of acidity in which neither of these two interferences are present and a maximum amount of BH^+ is present. Where it became difficult to determine the correct acidity calculations were made at wavelengths (370-450 m mu, usually) at which BH^+ absorbs very little; at these wavelengths the absorption of the solution containing approximately a maximum amount of BH^+ is small, and so the change of the absolute amount with acidity is negligible in comparison with the absorption of a solution containing an appreciable amount of the free base or the second ion at the same wavelength. This procedure eliminates error because only differences in absorption are involved in the calculation of both pK's. Experimental difficulties prevented the use of this procedure with two compounds, where $Y = NO_2$, OCH_3; the values obtained for these two at higher wavelengths are acceptable because they vary in a random manner with wavelength. It was noted with other compounds that there is not a random variation with wavelength at these higher wavelengths when the observed spectrum is not that obtained when the maximum amount of BH^+ is formed.

Tables 17 and 18 contain a compilation of pK_1 and pK_2, respectively, determined for the nine dyes at various acidities. Although the pH probably is not known exactly in the solutions containing alcohol, it is seen that there is only random variation in pK_1 values obtained at different pH values. For this reason it is assumed that an average of such random values may be used for purposes of comparison, although it is doubtful that such values of pK_1 are the correct absolute values. It is seen in Table 18 that there is also a random variation among pK_2 values when they are determined between 43.00 and 67.50 per cent sulfuric acid, and that there is a definite trend above and below these limits. From this it is concluded that the rate of change of H_+ with acidity is the same as the rate of change of H_o with acidity between these limits. It is assumed again, for purposes of comparison only, that the average of pK_2 values distributed in this random manner, may be determined. Since no average could be obtained where $Y = OCH_3$, NO_2, an estimate is made of what the averages for these two compounds would be if their pK_2 values would be measured within these limits of percentage given above. It is seen from Table 18 that it is not difficult to make this estimate.

In Tables 1-9 optical densities x 10^3 are given in the left column and the corresponding pK_1 values in the right column.

Table 1. Y = NO_2

pH mmu	6.75	3.58		2.89		2.75		1.96		4.115 N
500	437	444	1.90	461	1.76	483	1.94	588	1.85	781
510	429	438	1.90	460	1.77	488	1.94	618	1.84	569
520	407	415	1.81	438	1.73	461	1.86	596	1.78	884
530	366	374	1.80	398	1.74	424	1.88	558	1.78	852
540	311	318	1.77	342	1.75	364	1.86	488	1.76	773
550	248	253	1.73	270	1.71	284	1.80	366	1.65*	605
Ave. pK_1			1.82		1.74		1.88		1.80	

* omitted from average.

Table 2. Y = SCN

pH mmu	6.75	2.89		2.75		1.96		4.115 N
390	292	274	1.74	265	1.80	176	1.84	22
400	395	368	1.78	354	1.84	232	1.84	18
410	498	464	1.78	464	1.83	297	1.83	28
420	592	553	1.78	553	1.86	357	1.84	45
430	658	618	1.76	618	1.82	412	1.83	77
440	706	666	1.75	666	1.83	463	1.81	117
450	738	698	1.79	698	1.85	514	1.81	199
460	757	726	1.75	726	1.80	573	1.79	302
Ave. pK_1			1.77		1.83		1.82	

Table 3. Y = SeCN

pH mmu	6.75	2.89		2.75		1.96		4.115 N.
390	151	146	1.49	130	2.03	87	1.95	21
400	205	196	1.58	174	2.03	116	1.89	12
410	255	243	1.61	218	2.01	146	1.88	16
420	298	283	1.65	256	2.01	175	1.87	25
430	333	318	1.62	289	2.00	203	1.86	40
440	353	338	1.63	309	2.00	225	1.86	63
450	368	355	1.59	327	2.00	252	1.84	99
460	376	366	1.65	340	2.02	278	1.83	146
Ave.	pK_1		1.60		2.01		1.87	

Table 4. Y = I

pH mmu	6.75	2.89		2.75		1.96		4.115 N
390	58	39	1.93	46	2.24	32	1.98	7
400	75	53	2.00	59	2.22	38	1.97	5
410	92	67	1.97	73	2.21	47	2.02	8
420	103	83	1.97	83	2.19	55	1.99	10
430	111	101	1.95	91	2.16	59	2.02	13
440	114	103	2.01	94	2.18	64	2.01	19
450	117	107	1.99	98	2.18	69	2.02	27
460	116	107	2.01	99	2.20	74	2.03	38
470	108	102	1.99	96	2.21	79	2.02	54
Ave.	pK_1		1.98		2.20		2.01	

Table 5. Y = Cl

pH mmu	6.75	3.85		2.75		4.115 N.
380	452	424	2.70	387	2.01	30
390	615	573	2.73	530	1.98	18
400	791	741	2.69	669	2.03	22
410	910	865	2.58	788	1.96	34
420	1020	968	2.61	880	1.98	59
430	1050	1000	2.69	920	1.95	98
440	1120	1070	2.59	948	2.09	159
450	1120	1070	2.64	970	2.07	248
460	1060	1020	2.66	968	1.96	400
470	975	945	2.42*	908	1.99	527
Ave. pK_1			2.66		2.00	

Table 6. Y = H

pH mmu	6.75	3.58		2.89		2.75		1.96		4.115 N
370	470	446	2.36	400	2.19	360	2.30	190	2.25	47
380	654	617	2.38	552	2.18	493	2.29	248	2.22	25
390	843	793	2.39	707	2.22	634	2.28	316	2.21	22
400	1010	946	2.43	840	2.21	759	2.29	380	2.21	28
410	1120	1050	2.42	937	2.20	822	2.33	432	2.21	47
420	1150	1090	2.35	975	2.18	875	2.29	463	2.21	78
430	1140	1080	2.38	975	2.18	885	2.28	493	2.21	131
440	1120	1070	2.34	974	2.17	885	2.29	538	2.21	211
450	1080	1040	2.33	955	2.19	888	2.29	598	2.21	327
Ave. pK_1			2.38		2.19		2.29		2.22	

Table 7. Y = CH_3

	pH									
mmu	6.75	3.58		2.89		2.75		1.96		4.115
370	183	176	2.38	158	2.32	143	2.46	96	2.39	64
380	252	240	2.34	206	2.31	181	2.42	98	2.31	29
390	318	303	2.30	259	2.28	228	2.38	116	2.31	17
400	373	356	2.28	301	2.29	263	2.40	131	2.24	15
410	408	388	2.31	327	2.31	289	2.39	148	2.26	18
420	416	398	2.26	339	2.28	297	2.37	154	2.27	25
430	406	392	2.18	337	2.25	296	2.37	159	2.26	36
440	406	392	2.19	339	2.25	298	2.39	169	2.27	52
450	399	382	2.33	335	2.29	299	2.41	183	2.27	78
460	364	352	2.28	315	2.27	286	2.40	195	2.27	113
470	304	296	2.35	277	2.26	262	2.37	208	2.28	162
Ave.	pK_1		2.29		2.28		2.40		2.28	

Table 8. Y = $C(CH_3)_3$

pH mmu	6.75	3.58		2.89		2.75		1.96		4.115
380	273	261	2.30	233	2.19	206	2.34	105	2.33	33
390	350	333	2.31	293	2.21	258	2.33	125	2.28	17
400	415	394	2.32	344	2.22	307	2.32	147	2.26	14
410	457	434	2.32	378	2.23	338	2.32	164	2.26	17
420	469	449	2.25	392	2.21	349	2.32	172	2.27	25
430	464	444	2.27	389	2.22	349	2.32	179	2.26	36
440	462	443	2.27	392	2.21	352	2.32	192	2.26	55
450	453	437	2.24	389	2.21	352	2.33	206	2.26	83
460	419	405	2.28	367	2.22	338	2.33	223	2.26	125
470	356	348	2.26	328	2.17	308	2.36	241	2.24	181
Ave. pK_1			2.28		2.21		2.33		2.27	

Table 9. Y = OCH_3

pH mmu	6.75	3.58		2.89		2.75		1.96		2.058 N
480	1580	1520	2.37	1370	2.29	1270	2.38	868	2.29	538
510	299	343	2.34	473	2.33	550	2.41	865	2.34	1102
520	124	191	2.35	382	2.32	499	2.41	976	2.34	1329
530	50	132	2.35	363	2.32	512	2.41	1090	2.33	1533
540	17	108	2.34	372	2.32	533	2.40	1190	2.33	1687
550	6	101	2.34	376	2.33	542	2.40	1220	2.33	1738
560	2	96	2.33	371	2.32	538	2.39	1220	2.32	1748
Ave. pK_1			2.34		2.32		2.40		2.33	

In Tables 10-16 E values are given in the left column and $-pK_2$ in the right column   * omitted from average

Table 10. $Y = NO_2$

% H_2SO_4	36.00	70.67		74.55		77.55		79.00		97.00
H_o		-5.38		-5.90		-6.19		-6.40		
mmu										
360	3005	4810	6.09	9930	5.68	11500	5.68	13170	5.37	14120
370	1808	4440	6.08	11680	5.68	14100	5.65	16130	5.42	17640
380	1085	3980	6.16	13600	5.69	17000	5.62	19200	5.47	21320
390	792	3980	6.26	15500	5.68	19750	5.58	21990	5.55	24390
400	1049	4160	6.23	17200	5.65	22200	5.47	23810	5.43	26270
410	1930	4440	6.33	18000	5.63	23000	5.43	24000	5.48	26630
420	3523	5000	6.41	17500	5.63	22000	5.39	22460	5.52	24920
430	6202	6670	6.86*	15480	5.68	18800	5.43	19360	5.49	20990
440	10260			13700	5.71	15400	5.19*			15910
Ave. $-pK_2$			6.22		5.67		5.53		5.47	

Table 11. $Y = I$

% H_2SO_4	16.00	53.80		55.50		58.10		59.80	
H_o									
mmu		-3.41		-3.60		-3.91		-4.01	
380	1388	2610	4.15	2960	4.24	3680	4.34	5230	4.09
390	1040	2858	4.12	3200	4.22	4530	4.25	6000	4.11
400	1148	3748	4.05	3940	4.21	5400	4.27	7550	4.09
410	1634	5270	4.00	5680	4.13	7400	4.23	9700	4.09
420	2642	6780	4.02	7150	4.17	9850	4.38	12650	4.05
430	4270	8500	4.08	9600	4.15	12850	4.17	15800	4.05
440	6548	10780	4.12	12100	4.12	15850	4.16	18800	4.05
450	9654	13800	4.10	15000	4.15	18800	4.13	21700	4.02
Ave. $-pK_2$			4.08		4.17		4.21		4.07

Table 11. (continued)

% H_2SO_4	67.50		70.50		
H_o					
mmu	-4.95		-5.32		
380	7900	4.43	7746	4.84	9856
390	10200	4.30	9520	4.83	12260
400	13100	4.20	12940	4.60	15200
410	17000	4.13	16740	4.55	19520
420	21600	4.10	20520	4.57	23720
430	26100	3.98	24580	4.60	28440
440	30000	3.94	28280	4.59	32280
450	32300	3.82	30920	4.48	33960
Ave. $-pK_2$		4.06		4.56	

Table 12. Y = Cl

% H_2SO_4	27.00	54.00		59.00		62.00		65.00		97.00
H_o mmu		-3.44		-4.01		-4.25		-4.65		
360	2560	4260	3.73	5480	3.86	6700	3.66			7550
370	1163	4200	3.80	7110	3.84	8580	3.79	10650	3.36*	11140
380	700	4860	3.86	9300	3.88	11650	3.82	14450	3.60*	15680
390	750	6000	3.90	12200	3.91	15400	3.85	19130	3.70	21190
400	1165	7580	3.94	15800	3.92	19600	3.89	24720	3.75	27680
410	1800	9220	3.95	19300	3.92	24600	3.83	30040	3.72	33340
420	2900	11000	3.96	21600	3.94	28300	3.81	32570	3.87	37470
460	14600	15800	4.13	18400	3.94	19750	3.82	19980	4.16	21675
Ave.-pK_2			3.93		3.91		3.82		3.85	

Table 13. Y = H

% H_2SO_4	27.00	53.80		56.50		59.00		62.00		97.00
H_o mmu		-3.41		-3.72		-4.01		-4.25		
360	1350	5776	3.55	6980	3.68	8480	3.72	9650	3.73	12125
370	765	7320	3.58	8950	3.71	11150	3.76	12700	3.87	17040
380	635	8862	3.60	11300	3.70	14600	3.71	16400	3.76	21565
390	785	10250	3.63	13680	3.69	17600	3.70	20200	3.71	25780
400	1240	10720	3.70	15630	3.69	20300	3.79	22750	3.72	29040
410	1960	10575	3.75	16750	3.66	21400	3.65	24800	3.59	29820
420	3200	9890	3.84	16300	3.68	20600	3.65	24100	3.57	28240
430	5155	9280	4.00	15080	3.74	18400	3.67	21200	3.66	25360
440	7625	9640	4.04	13100	3.69	15000	3.66	16800	3.45	18260
Ave. -pK_2			3.73		3.69		3.70		3.67	

Table 14. Y = CH_3

% H_2SO_4	16.00	36.00		43.00		45.00		47.00	
H_o mmu		-1.64		-2.25		-2.40		-2.50	
380	1505	2018	3.11*	4866	2.81	5940	2.80	7370	2.72
390	984	2052	2.90	6098	2.73	7620	2.72	9610	2.64
400	1040	2496	2.87	7476	2.74	9500	2.73	12000	2.65
410	1330	3100	2.86	8730	2.75	11500	2.71	14650	2.62
Ave. $-pK_2$			2.93		2.76		2.74		2.66

Table 14. (continued)

% H_2SO_4	53.80		56.50		97.00
mmu	-3.41		-3.72		
380	12615	3.02	14640	2.99	17100
390	16655	2.90	19550	2.75	21545
400	21260	2.89	24400	2.83	27440
410	25560	2.85	28300	3.01	32230
Ave. $-pK_2$		2.92		2.89	

Table 15. Y = $C(CH_3)_3$

% H_2SO_4	16.00	43.00		45.00		47.00	
H_o mmu		-2.25		-2.40		-2.50	
380	930	4225	2.83	5300	2.82	6830	2.72
390	690	5230	2.79	6870	2.79	8820	2.71
400	860	6525	2.81	8570	2.80	11200	2.68
410	1250	7875	2.83	10480	2.79	13600	2.69
Ave. $-pK_2$			2.81		2.80		2.70

Table 15. (continued)

% H_2SO_4	53.80		56.50		96.95
H_o mmu	-3.41		-3.72		
380	14415	2.64	15200	2.74	16680
390	18950	2.63	20400	2.63	22000
400	23750	2.68	25800	2.66	27900
410	28100	2.67	31400	2.43*	32940
Ave. $-pK_2$		2.65		2.68	

Table 16. Y = OCH_3

% H_2SO_4	5.10	21.00		24.69		27.00	
H_o mmu		-0.65		-0.95		-1.10	
410	2895	3536	1.85	4860	1.60	5954	1.50
420	2680	4048	1.73	6260	1.55	7518	1.53
430	2575	4658	1.71	7660	1.56	9016	1.58
440	2895	5412	1.74	8540	1.64	10655	1.62
Ave. $-pK_2$			1.76		1.59		1.56

Table 16. (continued)

% H_2SO_4	36.00		96.95		
H_o mmu	-1.38		-1.64		
410	7500	1.41	10100	1.34	13730
420	10070	1.44	14180	1.39	20630
430	13300	1.53	19200	1.38	28300
440	16400	1.55	24100	1.40	36320
Ave. $-pK_2$		1.48		1.38	

Table 17. pK_1 values of the dyes at different pH's.

Y	3.85	3.58	2.89	2.75	1.96	Ave.	
NO_2		1.82	1.74	1.88	1.80	1.81	.04
SCN			1.77	1.83	1.82	1.81	.02
SeCN			1.60	2.01	1.87	1.83	.15
I			1.98	2.20	2.01	2.06	.09
Cl	2.66*			2.00		2.00	
H		2.38	2.19	2.29	2.22	2.27	.07
CH_3		2.29	2.28	2.40	2.28	2.31	.04
$C(CH_3)_3$		2.28	2.21	2.33	2.27	2.27	.03
OCH_3		2.34	2.32	2.40	2.33	2.35	.03

* Omitted from average.

Table 18. $-pK_2$ values of the dyes at different acidities

% H_2SO_4	NO_2	I	Cl	H	CH_3	$C(CH_3)_3$	OCH_3
21.00							1.76
24.69							1.59
27.00							1.56
31.56							1.48
36.00					2.93		1.38
43.00					2.76	2.81	
45.00					2.74	2.80	
47.00					2.66	2.70	
53.80		4.08	3.93^{t}	3.73	2.92	2.65	
55.50		4.17					
56.50				3.69	2.89	2.68	
58.10		4.21					
59.00			3.91	3.70			
59.80		4.07					
62.00			3.82	3.67			
65.00			3.85				
67.50		4.06					
70.50		4.56**					
70.67	6.22						
74.55	5.67						
77.55	5.53						
79.00	5.47						

Table 18. (continued)

Y	NO_2*	I		Cl		H		CH_3		$C(CH_3)_3$		OCH_3**
Ave.	7.00	4.12	.06	3.88	.04	3.70	.02	2.82	.1	2.73	.06	1.30

t Determined at 54.00 % H_2SO_4.

* Estimate of what this would be if measured in the middle range of acidity.

** Omitted from average.

Table 19. Electric moments of the dyes.

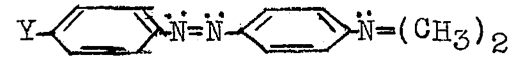
Y	mu (Debye)
NO_2	8.15
SeCn	6.85
SCN	6.65
Cl	4.75
I	4.66
H	3.01
CH_3	2.61
$C(CH_3)_3$	2.41
OCH_3	2.73

III. DISCUSSION OF RESULTS

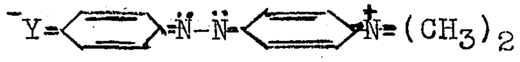
A. Summary of the results. The results given in Tables 17 and 18 may be summarized briefly. Both ionization constants are affected by the nature of the substituent, Y, in such a way that lists of pK_1 and pK_2, according to the magnitude of the value arrange the dyes in the same order. The order is, with the group that hinders the addition of protons most given first: SCN, NO_2, SeCN, I, Cl, H, CH_3, $C(CH_3)_3$, and OCH_3. The pK_1 values are much closer together than the pK_2 values; in the former they are so close that experimental error sometimes makes it impossible to determine the correct order. A similar order is obtained from a list of the electric moments of these dyes (11), given in Table 19. It is believed that in both kinds of measurements the group which hinders the addition of a proton most or makes possible the largest electric moment is the group which accepts electrons most easily. (In considering electric moments spatial considerations must also enter in with non-linear molecules; this fact is taken into account in Table 19 so that the values given actually list the substituents in the order of their tendency to accept electrons.) This is assumed because the positions of the nitro and the methoxy groups are in agreement with this theory; the electron accepting ability of the other groups is discussed later.

B. The positions of the first and the second added protons. It is necessary to decide where the first and second protons add to the dye molecule. Since at least some of the substituents are such that they could not accept a hydrogen atom, and since all nine dyes act very much alike in the number of color changes (as well as the nature of the corresponding spectra) noted with increasing acidity, it is believed protons add only to nitrogen atoms. In order to make a decision as to where the first proton is added to the molecule, all the resonance contributions of the free base, except different Kekule structures and very minor contributions, must be considered (unshared electrons on nitrogen atoms are shown):

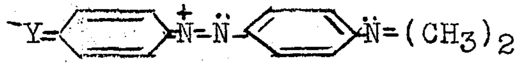
I.



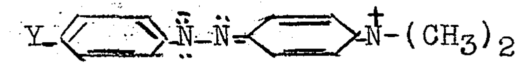
IV.



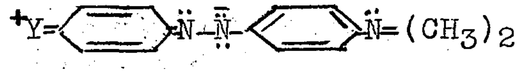
V.



VI.



VII.



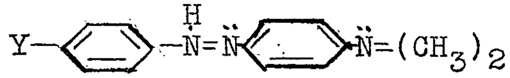
These five structures are not equally important. Examination of them makes it possible to decide where the first proton adds to the free base.

Y may be a good electron acceptor, but it is at best a poor electron donor to the ring. Structure VII is therefore relatively unimportant, since Y would have to be an electron donor in this structure. It is certain that the nitro group, at one extreme, is a much better electron acceptor than the methoxy group, at the other extreme, is an electron donor. The first proton does not add to the amino nitrogen because VI and (especially) IV are plainly important structures which would not be possible if the proton were to add to the amino nitrogen. It is seen below that there are structures analogous to IV and VI which contribute most to the stability of the first ion.

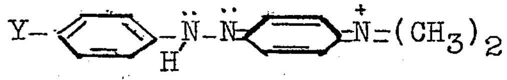
It then must be decided to which azo nitrogen the first proton adds. It is to be noted that the nature of Y partly determines the ease with which the first proton adds to the free base. Apparently Y does not affect the basicity of either azo nitrogen in I, IV, or VI as far as the resonance effect is concerned. The basicity of one or the other of the two azo nitrogens is affected by Y in V and VII; in both cases the better the electron acceptor, or the poorer the electron donor, the more difficult it is for the proton to add to the free base. Since V seems to be far more important than VII in almost all of the dyes in question, and since they all seem to behave in the same way, it is concluded that, according to V, the proton adds to the azo nitrogen nearer to the Y group. Since the groups which accept electrons will also attract oppositely charged bodies by the inductive effect, and since the inductive force decreases with distance, it is seen that this effect also tends to cause protons to add to the azo nitrogen nearer to the attracting group.

To determine the nitrogen to which the second proton adds it is necessary to consider all the resonance contributions to the structure of the first ion (except other Kekule structures and very minor structures):

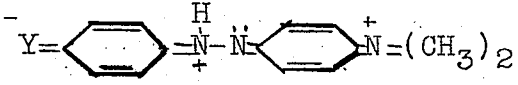
VIII.



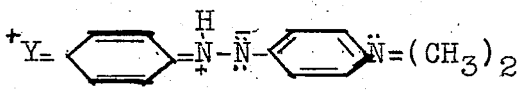
IX.



X.



XI.



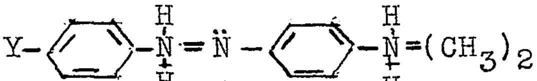
It is seen that VIII, IX, X, XI are analogous to I, VI, IV, and VII, respectively; no structure like V is possible.

Y affects the addition of the second proton very much in the same way as it affects the addition of the first proton. The inductive effect would favor the azo nitrogen farther from Y as compared to the amino nitrogen, but the inductive effect is probably not large over distances that are as great as these. Only X and XI may be used to decide the effect of Y due to resonance. It is concluded that X is much more important than XI because XI, as VII, is relatively unimportant, and X, as IV, is very important. For this reason it is believed the second proton adds to the amino nitrogen.

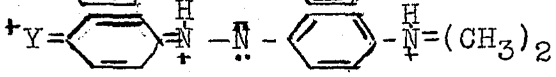
Since the amino nitrogen is much less electronegative than an azo nitrogen, it is probably true that X is relatively more important among structures of the first ion than V is among the contributions to the free base structure. Since it is these structures which determine the relative ease with which a proton is added, harmony with the fact that there is a much greater difference between the various pK_2 than between pK_1 values.

The only important structures, other than Kekule variations, to the structure of the second ion are these:

XII.



XIII.



C. The color of the free base, the first ion, and the second ion. The most important contribution to the structure of the free base undoubtedly is I; equivalent Kekule structures in each of the aromatic nuclei are possible only in I, and this stabilizes the structure. Of the others, IV is very likely the most important, because in IV both the amino nitrogen and Y have the charges most likely to produce stability. VI is more important than V, but the difference would not be pronounced where Y is a good electron acceptor.

One of the modern ideas on color, which is mentioned above, states that where there is a large separation of charge, light absorption takes place at a longer wavelength than is possible if there is a small separation of charge or no separation of charge at all. It may be that the color of the free base, yellow or orange, is due to IV, and, to a lesser extent, VI.

The most important structure of the first ion is VIII, since only in VIII can there be equivalent Kekule structures in both aromatic nuclei. But it must be remembered that all structures have a single positive charge, and it undoubtedly is easy for this positive charge to migrate. IX, therefore, is very important; X is as important here as IV is for the free base. It may well be that the deep red color of the first ion, as compared with the yellow color of the free base, is due to the importance of IX, where there is a separation of charge; the analogous structure for the free base, VI, is relatively not as important. VII and XI are probably unimportant.

For the second ion XII is undoubtedly far more important than XIII. XII is analogous to I, while XIII is analogous to VII. Here the positive charges on XII cannot migrate; there is not an easy separation of charge, and the ion is yellow.

D. The effect of structure on reactivity. Hammett (12) summarizes the effect of substituents on reactivity. It is found that for a series of compounds where one substituent is varied, as in the case of the dyes used in this work,

$$(12) \quad \log k - \log k^{o} = \rho\sigma$$

where k^{o} is the rate or equilibrium constant for the unsubstituted reactant, k is the rate or equilibrium constant for a substituted reactant, ρ is a constant for a series of substituents in a given compound, and σ is a constant determined by the nature of the substituent. σ is determined by observing the reactivity of a compound of a given substituent in a series where the other constants are determined; σ for a substituent is therefore arbitrary, but constant for that substituent in different compounds. Hammett records σ for all the substituents discussed in this work except Y = SCN and Y = SeCN.

Average pK_1 values and average pK_2 values are plotted against σ for the other seven substituents in Fig. 3. It is not necessary to consider $\log k^{o}$, since it is a constant; a straight line whose slope is ρ should be produced if (12) holds.

It is seen that this ρ-σ treatment yields fairly good results for pK_2 values, as compared to the poorer results for the pK_1 values. The pK_1 values of some pairs of compounds are close enough so that the limits of error overlap.

The order of pK_2 values is in better agreement with what would be expected than the order of the electric moments: where Y = I, the electric moment is less than

FIG. 3

σ, THE SUBSTITUENT CONSTANT, VS. pK, OF SEVEN RELATED AZO DYES

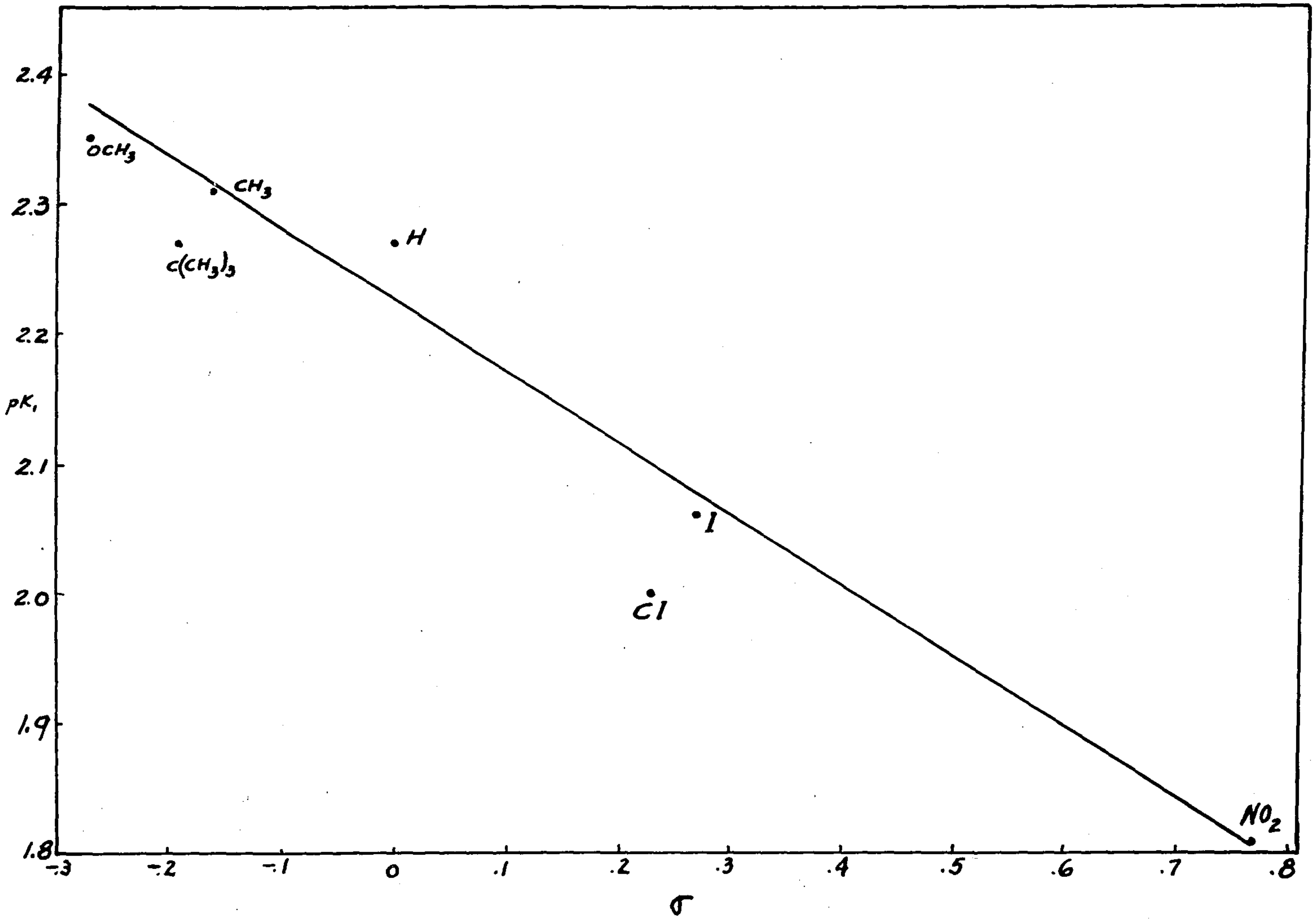
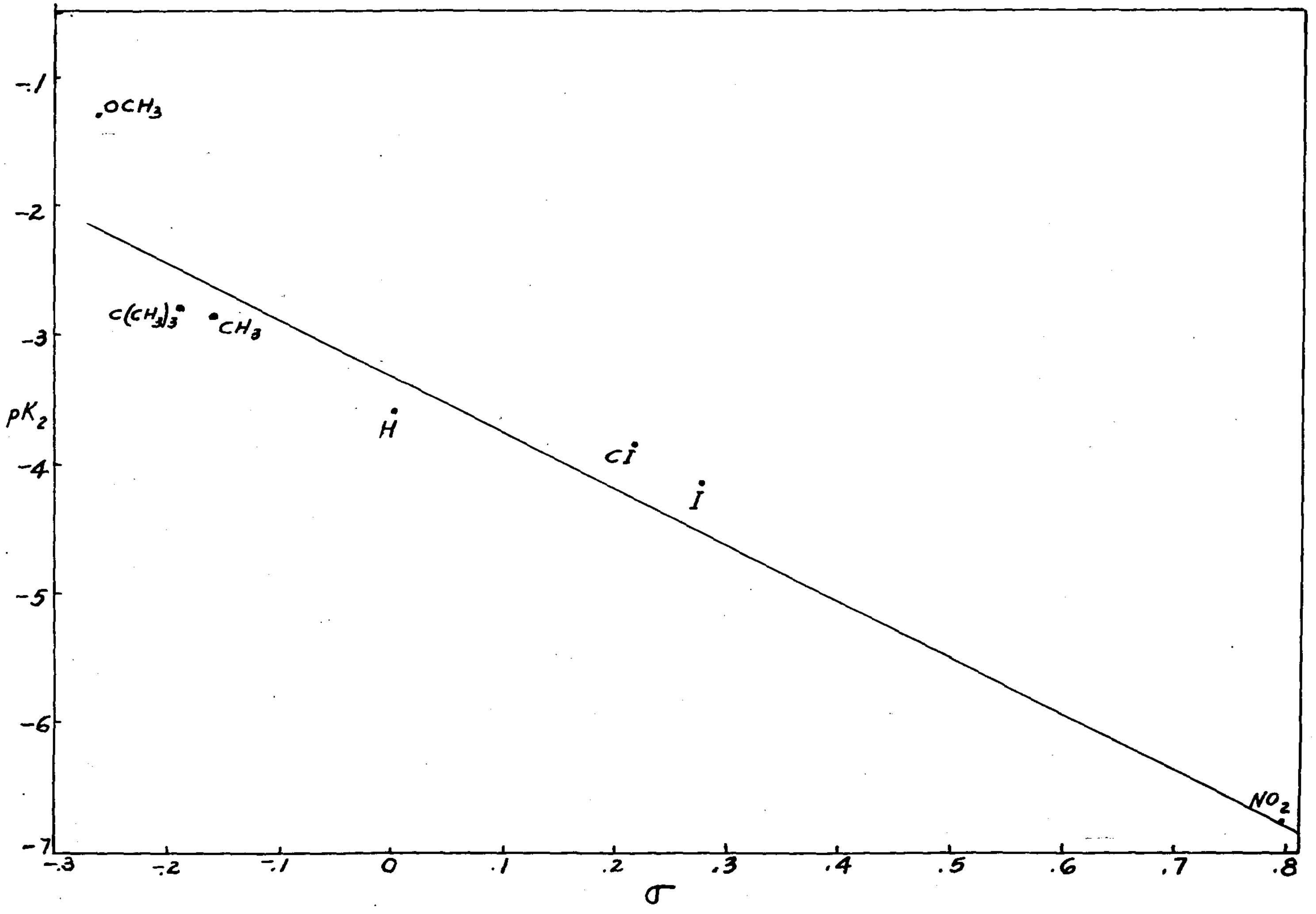


FIG. 4

σ, THE SUBSTITUENT CONSTANT, VS. pK_2 OF SEVEN RELATED AZO DYES



where Y = Cl; this is not in accord with the magnitude of the σ values tabulated by Hammett.

It was not possible to find pK_2 values for Y = SCN and Y = SeCN, since these compounds evidently slowly decomposed (as noted by the spectrum) in strong acid. However, there can be little doubt concerning the approximate position of these groups from the electric moments and pK_1 values. This is an unexpected, although interesting, result, since these groups are strong ortho-para orienting groups (13) and they would be expected to be near the other end of the list.

IV. SUMMARY

A. A spectrophotometric method for the determination of the relative ionization constants of the first and of the second ions of a series of nine homologous dyes has been used.

B. These data and the electric moment data have been used to determine the atoms to which the first and the second protons add, the relative importance of the principal resonance structures of these dyes, and the relative tendency of these nine substituent groups to accept electrons.

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