

A QUANTITATIVE STUDY OF THE ACIDITY OF CERTAIN HYDROCARBONS

By

Richard Eben Crocker

A THESIS

Submitted to the School for Advanced Graduate Studies
of Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

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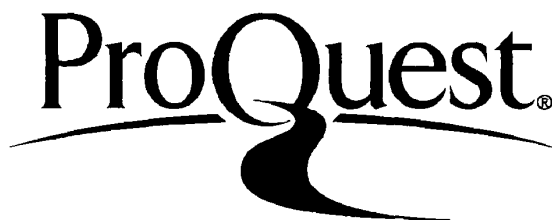
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To My Wife

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AN ABSTRACT

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ABSTRACT

The purpose of this investigation was to study the effect of structural changes on the acidity of the alpha-hydrogens of certain alkylaromatic hydrocarbons. When alkylaromatics are heated in the presence of a suitable catalyst such as potassium metal, hydrogens on the carbon alpha to the aromatic ring may exchange. This reaction was investigated as a possible method for determining the relative acidity of hydrocarbons.

A general procedure for the preparation of alpha-deuterated hydrocarbons was developed which resulted in little or no deuterium in the aromatic ring. The method involved cleavage of the appropriate aryl-alkyl methyl ether with potassium metal followed by hydrolysis of the organometallic with deuterium oxide. The following hydrocarbons were prepared in this manner: cumene- d_α , sec-butylbenzene- d_α , 3-phenylpentane- d_α , 2-phenylpentane- d_α , 2-methyl-3-phenylbutane- d_α and 2,2-dimethyl-3-phenylbutane- d_α . These standards were analyzed mass spectrometrically and then used for preparing infrared calibration curves from which unknown amounts of deuterium could be determined.

Separation of small volumes of hydrocarbon mixtures was accomplished by adapting a gas chromatography apparatus so that recovery of the individual components was near-quantitative.

The effects of several catalysts, temperature ranges, reaction vessels and compound types were studied. The exchange rates varied

directly with the amount of catalyst and are also dependent on the molar concentrations of the hydrocarbons. Conditions found most suitable for kinetic experiments involved heating two hydrocarbons with ethylbenzene- d_α for varying times at 150° in sealed tubes using potassium metal as the catalyst.

First order rate constants were obtained from plots of $\log (100/100-\%D)$ vs. t , where $\%D$ was the mole percent of deuterium in the hydrocarbon at time t . The order of decreasing relative exchange rates was found to be: cumene, 18.9; sec-butylbenzene, 8.13; 2-phenylpentane, 6.91; 3-phenylpentane, 1.96; 2-methyl-3-phenylbutane, 1.90; 2,2-dimethyl-3-phenylbutane, 1.00. This order parallels that of predicted acidity of these compounds.

Results obtained are consistent with a mechanism involving initial attack by potassium on the alpha-hydrogen of each competing hydrocarbon to form the organopotassium salt. This is followed by deuterium transfer between the carbanion portion of the salt and ethylbenzene- d_α . Attack by potassium is believed to be rate determining in the case of most of the hydrocarbons studied. Both paths are believed to be directly related to the acidity.

Diphenylmethane did not exchange protium for deuterium with ethylbenzene- d_α under a variety of conditions. An explanation for this is offered: An attempted competition reaction between cumene and phenylcyclopropane under the exchange conditions resulted in deuterium transfer to cumene but polymerization of phenylcyclopropane.

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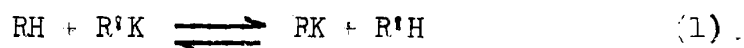
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INTRODUCTION

INTRODUCTION

This thesis is concerned with a study of the acidity of alpha-hydrogens in several alkylaromatic hydrocarbons. Before discussing the present work, however, it may prove useful to examine several previous, related studies which have been reported, including a list of hydrocarbons whose acidity has been investigated.

It has been generally accepted that organoalkali compounds exhibit salt-like character (1). Using Bronsted's definition of an acid, the hydrocarbon portion of such compounds is derived from an acid whose acidity must be of an extremely low order. The general method which has been utilized for measuring the acid strength of compounds of this type is the replacement of a weak acid by a stronger one. The work of Conant and Wheland (2) was the first attempt to assign pK_a values to a number of extremely weak organic acids. This they did by studying metathetical reactions between salts and acids, assuming the degree of dissociation of all salts to be approximately the same. It was only necessary to determine whether the reaction



proceeded from right to left or vice versa with each pair of acid and salt (R and R' are organic residues). Observation of the color of the solution, which is very characteristic for a number of metallic compounds, and carbonation of the reaction mixture followed by isolation of the resulting carboxylic acids were the two methods used for

determining on which side of the equation equilibrium lay. This study was later extended by McEwen (3) who used a spectroscopic method (using etioporphyrin I as an indicator and sodium triphenylmethyl as the base used to titrate the acid) and a polarimetric method (in which an optically active acid was used, equilibrium being determined with the aid of a polarimeter). Both of these studies assigned approximate values of strength on the basis of the equation

$$pK_1 - pK_2 = \log [(R_1^-)/(R_1H)] - \log [(R_2^-)/(R_2H)]$$

where pK_1 and pK_2 are the respective acid strengths, (R_1^-) and (R_2^-) are the concentrations of the respective anions and (R_1H) and (R_2H) are the concentrations of the corresponding acids. Conant and Wheland estimated that metathesis would proceed to 90% completion if the acids differed by two pK units. However, in the case of the colorimetric measurements, a five-fold excess of one reagent was used, resulting in a difference of 0.4 pK units corresponding to 90% completion. As a reference standard, Conant and Wheland chose the pK value of 20 for acetophenone while McEwen used the known value of 16 for methanol. Table I lists some of the results of these investigators.

Kleene and Wheland (4) extended this series to phenylcyclohexane and phenylcyclopentane. The order of decreasing acid strength was found to be diphenylmethane > phenylcyclopentane > cumene > phenylcyclohexane.

Bryce-Smith (5) has studied the acidity of several hydrocarbons by investigating the metalation of alkylbenzenes by alkyl-sodium and -potassium compounds. He found that the tendency for reaction at the

TABLE I

ACIDITY OF VARIOUS COMPOUNDS STUDIED BY CONANT AND
WHELAND (2) AND BY McEWEN (3)

Acid	pK	Acid	pK
Methanol	16	Fluorene	25
Isopropyl alcohol	18	Aniline	27
Ethyl alcohol		Diphenylbenzylmethane	31
Benzyl alcohol		Triphenylmethane	33
tert-Butyl alcohol	19	Diphenylmethane	35
Acetophenone		1,1-Diphenylpropene	36
Triphenylcarbinol		Cumene	37
9-Phenylfluorene	21	Ethane	40(?)
Indene			
Phenylacetylene			
Diphenylamine	23		

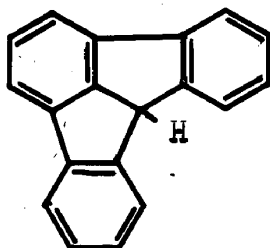
alpha-position of the side chain decreased in the order, toluene > ethylbenzene > cumene. He also determined isomer ratios for the metalation of cumene by ethylpotassium, n-propylpotassium, n-amylopotassium and n-amylsodium, discovering that the meta-isomer always predominated. From the data obtained in the competitive metalation of benzene and cumene by ethylpotassium, partial rate factors were calculated from which it was concluded that, qualitatively, each hydrogen atom in cumene was less acidic than a hydrogen atom in benzene, the order of decreasing acidity being para > meta > alpha > ortho > > beta.

Considerable work has been appearing in the Soviet literature since 1950 dealing with deuterium exchange as a method for comparing the strength of very weak acids. The bulk of this work has been done by Shatenshtein (6,7), who determined the amount of exchange for a number of hydrocarbons in D_2O , ND_3 and NB_3 containing potassium amide at various temperatures. Included in the list of compounds studied were benzene, toluene, indene, fluorene, triphenylmethane, diphenylmethane, acenaphthene and naphthalene. Shatenshtein pointed out the parallelism between the first order rate constants which he obtained and the ionization constants of Conant and Wheland (2). A somewhat similar procedure was followed by Roberts (8) who determined the exchange rates of various o-, m- and p-deuterated benzene derivatives with potassium amide in liquid ammonia. The results were interpreted on the basis of the relative acidity of the various aromatic hydrogens.

While the method of deuterium-protium exchange in hydrocarbons in basic media has been little used until recent years, exchange in acid media has been extensively studied. A large volume of work concerned with deuterium exchange of aliphatic and aromatic hydrocarbons in deuteriosulfuric acid has appeared in the literature, much being done by Ingold and Wilson (9), Stevenson (10), Burwell (11) and Gold (12,13). Shatenshtein (14,15) has also studied the deuterium exchange of a number of aromatic hydrocarbons in liquid hydrobromic acid containing deuterium bromide and determined first order rate constants for the various hydrogen atoms on the aromatic ring. Some compounds included in this work were benzene, toluene, ethylbenzene, cumene, tert-butylbenzene,

n-butylbenzene, n-propylbenzene, 3-phenylpentane, diphenylmethane, triphenylmethane, naphthalene and fluorene. It was found in the case of the alkylbenzenes that all ring- and alpha-hydrogens were exchanged for deuterium, although hydrogens further removed from the aromatic ring were not.

Recently, Rapoport and Smolinsky (16) reported the synthesis of fluoradene



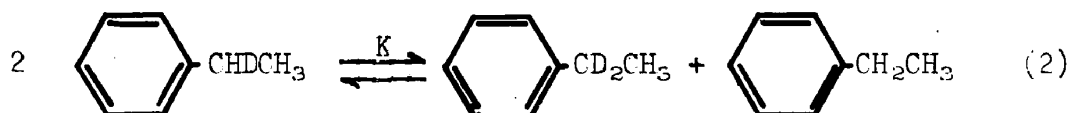
which contains an unusually acidic hydrogen. This compound could be removed from benzene by washing with dilute aqueous alkali and exchanged hydrogen for deuterium in boiling deuterium ethoxide. It has a pK_a value of 11 ± 0.5 .

Another example of the acidic properties of alpha-hydrogens in alkylaromatic compounds is the work of de Postis (41) who reported that cesium metal liberates hydrogen from toluene.

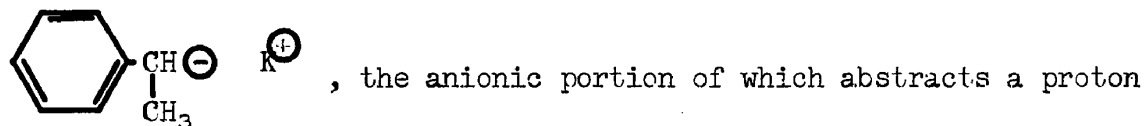
It is apparent from the foregoing discussion that, although the relative acidity of a wide variety of hydrocarbons has been determined, the bulk of the work is qualitative. Also, previous investigators have limited themselves mainly to compounds with relatively large differences in acidity, due, in part, to the lack of a sensitive method for determining small variations.

The present study was prompted by the discovery that alpha-hydrogens of alkylaromatics exchange at measurable rates in the presence of reactive alkali metals, metal hydrides and other bases (17).

For example, ethylbenzene- d_α , when refluxed over potassium metal, disproportionated to ethylbenzene- $d_{\alpha,\alpha}$ and ordinary ethylbenzene.



Presumably an organometallic compound is produced in small quantity



(or deuteron) from the alpha carbon atom of another hydrocarbon molecule.

In this way exchange occurs.

If the anionic species could select between two sources of alpha protons, presumably it would obtain the proton from the more acidic source. The relative rates of deuterium exchange of two hydrocarbons might furnish, then, a method for measuring their acidities.

The purpose of this investigation was to determine by this method the effect of structural changes on the acidity of the alpha-hydrogen of certain alkylaromatics. Briefly, this involved the syntheses of various alkylaromatics, allowing two non-deuterated hydrocarbons to compete for the deuterium of a deuterated species in the presence of an appropriate catalyst, separation of the components and analyses for deuterium content from which exchange rates were calculated. The experimental section which follows contains details of the syntheses and exchange procedure, including the analytical and separation techniques. Examples of the rates obtained and a discussion concerned with an interpretation of these data are given in the section on results and discussion. In the appendix calibration curves and exchange results and rates are given.

EXPERIMENTAL

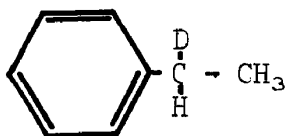
EXPERIMENTAL

A. Syntheses

The deuterated hydrocarbons were synthesized by three general methods: (A) reduction of suitable compounds with lithium aluminum deuteride and lithium deuteride, (B) reaction of the appropriate Grignard reagent with deuterium oxide and (C) cleavage of α -phenylalkyl methyl ethers with metallic potassium followed by hydrolysis with deuterium oxide.

In instances where the non-deuterated hydrocarbons were not available commercially, they were synthesized, usually by methods different from those required to make the corresponding α -deuterated compound. The preparation of each ordinary hydrocarbon is immediately followed by the synthesis of its deuterated counterpart.

Ethylbenzene- d_α (Procedure A)

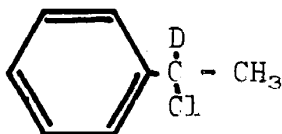


Ethylbenzene- d_α was prepared according to the method of Eliel (18). A 250-ml. round-bottomed flask was equipped with a reflux condenser protected with a drying tube, a 125-ml. addition funnel, a dry argon inlet and a Tru-bore stirrer with a Teflon blade. Into this vessel was pipetted 75 ml. of tetrahydrofuran (distilled from potassium hydroxide

and then freshly distilled from lithium aluminum hydride) followed by 1.1 g. (0.026 mole) of lithium aluminum deuteride (Metal Hydrides Inc., 98+% purity) and 3.2 g. (0.38 mole) of lithium deuteride (Metal Hydrides Inc., 98% purity). Then, without waiting for the slurry to dissolve, 34.5 g. (0.245 mole) of α -phenethyl chloride (19) was added with stirring. No marked exothermic reaction was noted. The reactants were stirred at gentle reflux for twenty-four hours, after which the reaction mixture was allowed to cool to room temperature. The excess hydrides were removed by the dropwise addition of a solution of 20 ml. of water in 30 ml. of tetrahydrofuran. The mixture was poured onto 100 g. of ice and 20 ml. of sulfuric acid. The bottom aqueous layer was separated and extracted with 100 ml. of pentane which was combined with the original organic layer. These were washed successively twice with 100 ml. of water, four times with 100 ml. of 85% ortho phosphoric acid, twice with 100 ml. of water, once each with 100 ml. of 10% potassium carbonate solution and 100 ml. of water. The organic layer was dried overnight over 10 g. of anhydrous calcium chloride, then fractionally distilled through a small glass helices-packed column. There was obtained 21.4 g. (82%) of ethylbenzene- d_{α} , b.p. 132.5° (731 mm.), $n_D^{20} = 1.4950$. Mass spectrometric analysis indicated $d_1 = 98.5 \pm 0.1\%$, $d_0 = 1.5 \pm 0.1\%$ and no deuterium atoms in the beta positions.

Ethylbenzene- $d_{\alpha,\alpha}$ (Procedure A)

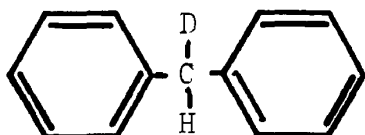
(a) Preparation of α -phenethyl chloride- d_{α}



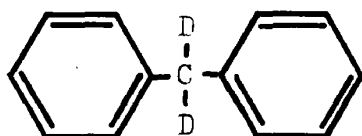
The reaction vessel described in the preparation of ethylbenzene- d_α was used. To an ice-cooled mixture of 0.8 g. (0.02 mole) of lithium aluminum deuteride in 25 ml. of dry tetrahydrofuran was added dropwise with stirring 8.0 g. (0.067 mole) of acetophenone. The mixture was then heated at reflux for twenty minutes, after which the mixture was cooled and 20 ml. of water slowly added dropwise. Layers were separated, the aqueous layer extracted twice with 50 ml. of ether and the combined organic layers washed successively with 30 ml. each of water, 10% sodium carbonate solution and water. After drying overnight over 6 g. of anhydrous magnesium sulfate, the ether was removed by distillation and the α -phenethyl alcohol- d_α which remained, without further purification, was added dropwise to 16 g. (0.14 mole) of thionyl chloride. The mixture was allowed to stand for four hours, then fractionally distilled using a small glass helices-packed column. The α -phenethyl chloride- d_α thus obtained weighed 6.9 g. (73%), b.p. $93-6^\circ/40$ mm., $n_D^{25.3} = 1.5212$.

(b) Reduction of α -phenethyl chloride- d_α

The procedure described in the preparation of ethylbenzene- d_α was followed. From 6.9 g. (0.049 mole) of α -phenethyl chloride- d_α , 0.8 g. (0.09 mole) of lithium deuteride and 0.2 g. (0.005 mole) of lithium aluminum deuteride, there was obtained 3.1 g. (59%) of ethylbenzene, b.p. $133-4^\circ/46$ mm., $n_D^{25} = 1.4954$. Mass spectrometric analysis showed $d_2 = 96.6 \pm 0.1\%$; $d_1 = 3.4 \pm 0.1\%$; $d_0 < 0.1\%$; no beta-deuterium atoms.

Diphenylmethane- d_α (Procedure A)

Using the procedure described in the preparation of ethylbenzene- d_α , 20.3 g. (0.10 mole) of benzhydryl chloride (prepared in 86% yield from benzhydrol and thionyl chloride), 1.3 g. (0.16 mole) of lithium deuteride and 0.4 g. (0.01 mole) of lithium aluminum deuteride after reaction yielded 4.0 g. (24%) of sym-tetraphenylethane, m.p. 208° (recrystallized from chloroform), and 8.3 g. (50%) of diphenylmethane, b.p. $100^\circ/3$ mm., $n_D^{20} = 1.5767$. The infrared spectrum of the sym-tetraphenylethane indicated the absence of any deuterium atoms. Mass spectrometric analysis showed the diphenylmethane- d_α to contain $d_1 = 95.8\%$, $d_0 = 4.2\%$.

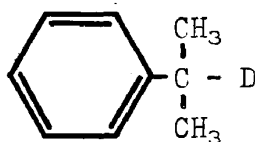
Diphenylmethane- $d_{\alpha,\alpha}$ (Procedure A)

The first attempt to prepare diphenylmethane- $d_{\alpha,\alpha}$ was by the reduction of benzophenone dichloride with lithium aluminum deuteride and lithium deuteride. Benzophenone dichloride was obtained in 80% yield from the reaction of benzophenone and phosphorous pentachloride (20). The general procedure cited in the preparation of ethylbenzene- d_α was followed. A small amount of liquid boiling from $95-125^\circ/3$ mm. was collected which was not further identified although the infrared spectrum

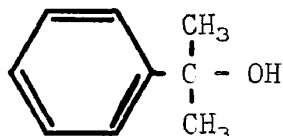
was recorded. Considerable solid material remained which, upon several recrystallizations from benzene, produced a 20% yield of white solid, m.p. $219-20^{\circ}$ and believed to be tetraphenylethylene (lit. m.p. $220-1^{\circ}$ (21)).

Diphenylmethane- $d_{\alpha,\alpha}$ was successfully prepared using a procedure similar to that of ethylbenzene- $d_{\alpha,\alpha}$ by reduction of benzophenone with lithium aluminum deuteride to form benzhydrol- d_{α} followed by conversion with thionyl chloride to benzhydryl chloride in 81% yield from benzophenone. The benzhydryl chloride- d_{α} was reduced with lithium deuteride and lithium aluminum deuteride to diphenylmethane b.p. $124^{\circ}/10$ mm., $n_D^{20} = 1.5771$, in 59% yield, mass spectrometric analysis: $d_2 = 91.7\%$, $d_1 = 6.7\%$, $d_0 = 1.6\%$. Also, after recrystallization from chloroform, a 9% yield of sym-tetraphenylethane, m.p. $206.5^{\circ}-207.0^{\circ}$, was obtained whose infrared spectrum indicated the presence of a C-D absorption peak.

Cumene- d_{α} (Procedure A)



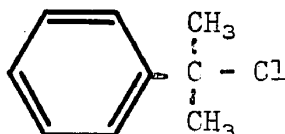
(a) Preparation of dimethylphenylcarbinol



To the Grignard reagent prepared from 9.0 g. (0.37 mole) of magnesium turnings and 46.2 g. (0.325 mole) of methyl iodide in anhydrous

ether was added dropwise 42.0 g. (0.350 mole) of acetophenone in 40 ml. of absolute ether. After decomposition with a solution of 70 g. of ammonium chloride in 200 ml. of water and work-up with 4% sodium bisulfite solution, there was obtained 35.3 g. (80%) of the white, low-melting solid carbinol, b.p. $53-5^{\circ}/1.5$ mm.

(b) Preparation of dimethylphenylcarbinyll chloride



Dimethylphenylcarbinyll chloride (22) was prepared by the addition of hydrogen chloride at 0° to dimethylphenylcarbinol in 67% yield and also to alpha-methylstyrene (23) in 63% yield, b.p. $53-6^{\circ}/1.2$ mm., $n_D^{20} = 1.5212$.

(c) Attempted reduction of dimethylphenylcarbinyll chloride

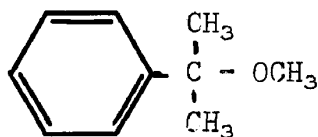
Several routes for preparing cumene- d_4 were investigated. In model experiments ordinary cumene was prepared in 10% yield from the reaction of phenyllithium with isopropyl bromide, 61% yield from benzene, isopropyl bromide and aluminum chloride (24) and 43% yield from the reduction of dimethylphenylcarbinyll chloride with lithium hydride and lithium aluminum hydride.

Cumene- d_4 was prepared by two methods, the first being the reduction of dimethylphenylcarbinyll chloride with lithium deuteride and lithium aluminum deuteride following the procedure outlined in the preparation of ethylbenzene- d_4 . This resulted in a mixture of

cumene- d_α and α -methylstyrene, which, after investigating separation methods including chromatography with silica gel and oxidation by cold potassium permanganate, was separated by bromination of the α -methylstyrene in the dark using carbon tetrachloride as solvent. Since only a 12% yield of cumene- d_α , b.p. $58^\circ/27$ mm., $n_D^{20} = 1.4918$, was realized after this purification procedure, the following, more general method was employed which is similar to that of Brown's (25).

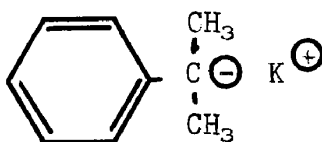
Cumene- d_α (Procedure C)

(a) Preparation of 2-methoxy-2-phenylpropane



The general procedure of Ziegler (26) was followed wherein α -methylstyrene and methyl alcohol in a 1:2 molar ratio were allowed to stand with several drops of 70% perchloric acid at 50° for 48 hours. A dilute solution of sodium hydroxide was then added and the organic layer separated, washed with water, dried over anhydrous sodium sulfate and distilled. A 62% yield of 2-methoxy-2-phenylpropane, b.p. $78^\circ/13$ mm., was obtained.

(b) Preparation of α -phenylisopropyl potassium



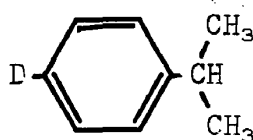
The method of Ziegler (26) was followed. A 500-ml. three-necked round-bottomed flask equipped with a reflux condenser protected with a drying tube, a thermometer, addition funnel, dry argon inlet and a high-speed stirrer was swept overnight with dry argon and also heated with a free flame to assure riddance of water. Using a pipette, 200 ml. of heptane (freed from olefins and water by treatment with potassium permanganate, concentrated sulfuric acid, drying, distillation and storage over sodium metal) and 14.8 g. (0.38 mole) of potassium metal (freshly cut under heptane) were added to the reaction flask. The mixture was heated with an electric mantle to 65° . When most of the potassium metal had melted, the stirrer was turned on and 30.0 g. (0.20 mole) of 2-methoxy-2-phenylpropane was added dropwise over a ninety-minute period. The color of the mixture changed from the initial grey-metallic through cinnamon to a deep maroon. The temperature of the reaction mixture was maintained between $64-72^{\circ}$ throughout this period. The mixture was stirred at 70° for six hours, then allowed to cool to room temperature. When the stirring was stopped, the finely-divided wine-colored organometallic began to settle out. The α -phenylisopropyl potassium was not further isolated but used in situ for the preparation of cumene- d_6 .

(c) Hydrolysis of α -phenylisopropyl potassium

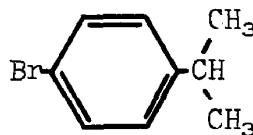
To the flask containing α -phenylisopropyl potassium was added dropwise over thirty minutes a solution of 8.2 g. (0.45 mole) of deuterium oxide ($> 99.5\%$ D_2O , obtained from the Stuart Oxygen Co., San Francisco)

in 75 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) with stirring. The white mixture was allowed to stand overnight under a blanket of dry argon. The following morning the mixture was heated at gentle reflux and stirred for thirty minutes. Then 20 ml. of water was added and the white, solid potassium deuterioxide dissolved. The bottom aqueous layer was extracted with 50 ml. of pentane and the combined organic layers dried overnight over 15 g. of anhydrous calcium chloride. The colorless solution was then distilled, the fraction boiling at 150.5° (738 mm.) being collected. A yield of 13.1 g. (57%) of cumene, $n_D^{20} = 1.4903$, was obtained. Mass spectrometric analysis showed it to contain $d_1 = 82.6\%$, $d_0 = 17.4\%$, no beta-deuterium.

Cumene- d_p (Procedure B)



(a) Preparation of p-bromocumene



The procedure of Bruce and Todd (27) was followed. To an ice-cooled mixture of 45.0 g. (0.337 mole) of bromobenzene and 2.2 g. (0.016 mole) of powdered anhydrous aluminum chloride was slowly (thirty minutes) added with stirring 15 g. (0.19 mole) of isopropyl chloride. The orange reaction mixture was heated on a steam bath for twenty

minutes. The deep-red mixture was poured onto 40 g. of ice and the lower milky layer separated and washed with concentrated sulfuric acid eight times (until the acid layer became only slightly colored). The organic layer was then washed successively with water, dilute sodium bicarbonate solution and water. After drying overnight over 5 g. of anhydrous calcium chloride, the mixture was distilled and 29.7 g. (79%) of *p*-bromocumene was collected, boiling at $95-8^{\circ}/9$ mm., $n_D^{20} = 1.5470$ (literature values: b.p. $89^{\circ}/10$ mm., $n_D^{20} = 1.5362$ (28); b.p. $97-8^{\circ}/5$ mm., $n_D^{20} = 1.5569$ (56)).

(b) Preparation and hydrolysis of the Grignard reagent from *p*-bromocumene.

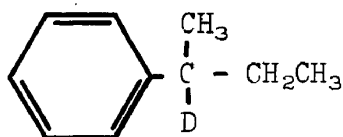
This procedure was patterned after the method described by Hart (17). In a dry 250-ml. three-necked flask equipped with a dry nitrogen inlet, addition funnel, stirrer and reflux condenser fitted with a drying tube was placed 2.4 g. (0.10 mole) of magnesium turnings and 20 ml. of dry ether. Then a solution of 30 ml. of ether and 20 g. (0.10 mole) of *p*-bromocumene was added dropwise so as to keep the reaction mixture at gentle reflux. After this addition the mixture was refluxed for one hour and then cooled with an ice bath. A solution of 6.0 g. (0.33 mole) of deuterium oxide (98+% D_2O , Stuart Oxygen Co., San Francisco) in 50 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added dropwise over a thirty-minute period. The reaction mixture was refluxed two hours, allowed to stand overnight and refluxed again one hour. After cooling, the bottom aqueous layer was separated and extracted with two 50-ml. portions of ether. The combined organic

layers were dried overnight (anhydrous calcium chloride) and distilled through a short Vigreux column. The fraction which boiled from 140-155° was redistilled through a small glass helices-packed column; the fraction boiling at 148-151° weighed 11.7 g. (97%), $n_D^{20} = 1.4892$, and the mass spectrometric analysis showed: $d_1 = 82.7\%$, $d_0 = 17.3\%$, no beta-deuterium.

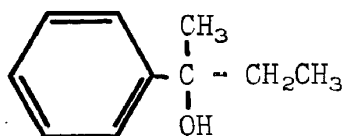
Oxidation of p- and α -deuterocumenes

In order to establish unequivocally the side chain and ring deuteration of these cumenes, they were oxidized to benzoic acid. The procedure given in Organic Syntheses (29) was followed using 10 ml. of concentrated nitric acid, 30 ml. of water and 2.0 g. (0.016 mole) of cumene (p- or α -deutero). The benzoic acid was produced in approximately 50% yield, white needles recrystallized from water, m.p. 122°. Oxidations of cumene using alkaline potassium permanganate or sulfuric acid-sodium dichromate resulted in very low yields of benzoic acid; the latter method was believed particularly poor due to the known ability of sulfuric acid to cause deuterium exchange (9).

sec-Butylbenzene- d_4 (Procedure C)

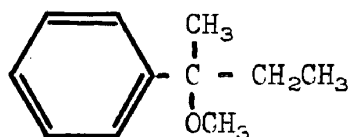


(a) Preparation of 2-phenyl-2-butanol



This was prepared using a procedure similar to that described in the preparation of 2-phenyl-2-pentanol. To the Grignard reagent prepared from 25.0 g. (1.03 moles) of magnesium turnings and 150 g. (0.96 mole) of ethyl iodide was added 60 g. (0.50 mole) of acetophenone. The 2-phenyl-2-butanol thus produced was fractionally distilled and 56.0 g. (75%) collected, b.p. 65-6°/2.0 mm., $n_D^{20} = 1.5187$ (literature value $n_D^{22} = 1.5158$) (22).

(b) Preparation of 2-methoxy-2-phenylbutane



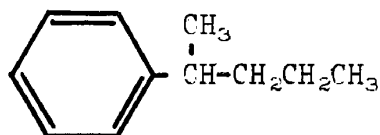
The procedure used was similar to that employed by Wallis (30) and Conant (31). In a 500-ml. round-bottomed flask was placed 60.0 g. (0.40 mole) of 2-phenyl-2-butanol, 100 ml. (2.5 moles) of methanol and 3.6 ml. of concentrated sulfuric acid. The mixture was allowed to stand overnight at room temperature. Ether (100 ml.) was added to the mixture, followed by 100 ml. of saturated sodium carbonate solution. The liquid was decanted from the sodium carbonate which precipitated, and the ether and some methanol removed on a steam bath. The bottom aqueous layer thus formed was separated and extracted using two 100-ml. portions of ether. The combined organic layers were filtered through anhydrous magnesium sulfate and dried overnight over 20 g. of anhydrous magnesium sulfate. The mixture was distilled in vacuo, 44.4 g. (68%) of 2-methoxy-2-phenylbutane being obtained, b.p. 66-7°/5.0 mm.,

$n_D^{25} = 1.4968$ (literature values: b.p. $63-5^\circ/2-3$ mm. (30), $n_D^{25} = 1.4981$, 1.4991 (32)).

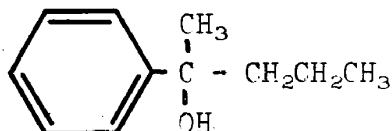
(c) Cleavage and hydrolysis of 2-methoxy-2-phenylbutane.

Following the procedure outlined in the preparation of cumene- d_4 , 14.8 g. (0.38 mole) of potassium metal and 32.9 g. (0.20 mole) of 2-methoxy-2-phenylbutane were allowed to react for seven hours at 68° followed by the addition of 8.2 g. of deuterium oxide. The sec-butylbenzene thus produced was distilled, fractions being collected boiling at $74^\circ/27$ mm., $n_D^{20} = 1.4894$. The yield was 16.5 g. (64%); mass spectrometric analysis showed: $d_1 = 46.6\%$, $d_0 = 53.4\%$, no beta- or gamma-deuterium atoms.

2-Phenylpentane



(a) Preparation of 2-phenyl-2-pentanol



The procedure was similar to that described for dimethylphenylcarbinol. The Grignard reagent prepared from 75.0 g. (0.96 mole) of n-propyl chloride and 25.0 g. (1.03 mole) of magnesium turnings in ether was treated at 0° with 60.0 g. (0.50 mole) of acetophenone in

dry ether. After stirring at gentle reflux for four hours and work-up with water (not acid), there was obtained 66.6 g. (81%) of 2-phenyl-2-pentanol, b.p. $74-6^{\circ}/2.1$ mm., $n_D^{20} = 1.5133$ (literature value: $112-3^{\circ}/14$ mm.) (22).

(b) Dehydration of 2-phenyl-2-pentanol and hydrogenation of resulting olefins.

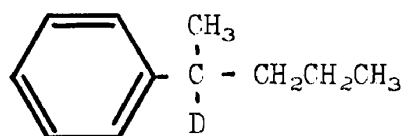
A modification of the method of Huston and Kaye (33) was used.

2-Phenyl-2-pentanol was dehydrated by heating at reflux and collecting the water formed in a distilling receiver. After removal of the water layer and drying over anhydrous calcium chloride overnight, the reaction mixture was distilled. 2-Phenyl-2-pentene (and isomers), b.p. $106-110^{\circ}/40$ mm., was obtained in 74% yield (based on acetophenone; the 2-phenyl-2-pentanol was not purified in this preparation).

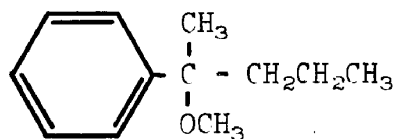
This olefin was then partially reduced by adding 40 g. (1.7 mole) of sodium metal to a solution of 37 g. (0.25 mole) of olefin in 375 ml. of absolute ethanol. After the sodium had reacted, 300 ml. of water was added, the resulting layers separated, the bottom aqueous layer extracted with three 100-ml. portions of ether and the combined organic layers washed with 100 ml. of saturated sodium chloride solution. The resulting light yellow solution was shaken with 200 ml. of cold saturated potassium permanganate for thirty seconds, 20 g. of sodium bisulfite added and the layers separated. The water layer was extracted twice with ether and the combined organic layers dried over 15 g. of anhydrous sodium sulfate. The dried mixture was fractionally distilled through a monel helices-packed column, 31 g. (84%) being collected at

67.5-68.0°/9 mm., $n_D^{20} = 1.4927$. However, when a sample of this product was put through gas chromatography apparatus, the presence of a small amount of slightly higher boiling impurity was apparent. This was probably 2-phenyl-2-pentene, an authentic sample of which, when put through the gas chromatography apparatus under the same conditions, caused a peak to be recorded at the same time interval as the impurity. To remove this olefin, the mixture was placed in a 500-ml. hydrogenation bottle and 120 ml. of absolute ethanol with 0.118 g. of platinum dioxide was added. After three and one-half hours of hydrogenation, the pressure had dropped from 51.0 to 45.0 p.s.i. and ceased to decrease. Work-up gave 24.2 g., b.p. 187-8° (744 mm.), $n_D^{20} = 1.4879$ (literature value: $n_D^{20} = 1.4876$)(28), of chromatographically-pure 2-phenylpentane.

2-Phenylpentane-d₁ (Procedure C)



(a) Preparation of 2-methoxy-2-phenylpentane



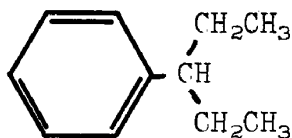
This was prepared in 56% yield from 50.0 g. (0.30 mole) of 2-phenyl-2-pentanol, 120 ml. (3.0 moles) of methanol and 2.6 ml. of sulfuric acid as described in the preparation of 2-methoxy-2-phenylbutane.

Product boiling from $66-9^{\circ}/2.4$ mm., $n_D^{20} = 1.4959-1.4982$, was collected.

(b) Cleavage and hydrolysis of 2-methoxy-2-phenylpentane.

The same procedure as that used for preparing cumene- d_4 was employed. After 8.2 g. (0.21 mole) of potassium metal and 19.6 g. (0.11 mole) of 2-methoxy-2-phenylpentane had been permitted to react at 68° for twelve hours, 5.0 g. (0.25 mole) of deuterium oxide was added. The 2-phenylpentane thus produced was distilled, the fraction collected boiling at $73^{\circ}/12$ mm., $n_D^{20} = 1.4880$, $n_D^{25} = 1.4857$, weighed 10.0 g. (64%). Mass spectrometric analysis showed: $d_1 = 64.1\%$, $d_0 = 35.9\%$, no beta-, gamma- or delta-deuterium atoms.

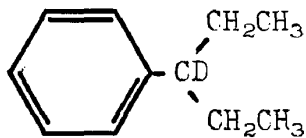
3-Phenylpentane



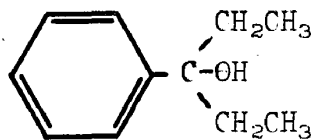
A procedure similar to that of Pines, Vesely and Ipatieff (34) was followed. In a typical run, a 200-ml. stainless-steel Magne-Dash autoclave was charged with 46 g. (0.50 mole) of toluene, 0.89 g. (0.023 mole) of potassium metal and 4.4 g. (0.18 mole) of sodium hydride. The autoclave was flushed several times with dry nitrogen. Ethylene was then added to a pressure of 810 p.s.i. (by the loss in weight of the ethylene tank, it was determined that 31 g. (1.1 moles) of ethylene was added), the magnetic stirrer adjusted to operate at moderate speed and the autoclave heated electrically to 190° . After eight hours, the

pressure had dropped to 640 p.s.i. The autoclave was vented and a stream of nitrogen passed through for several hours. After the mixture in the bomb was filtered through glass wool and 100 ml. of benzene used to rinse the autoclave and glass wool, the filtrate and benzene washings were washed with 100 ml. of water, dried overnight over 10 g. of anhydrous calcium chloride and distilled at reduced pressure through a glass helices-packed column. Fractions were collected which corresponded to toluene, n-propylbenzene, 3-phenylpentane and 3-ethyl-3-phenylpentane. A fraction boiling at $53-8^{\circ}/6$ mm., weighing 9.1 g. (12%), $n_D^{20} = 1.4884$ (literature value: $n_D^{20} = 1.4877$) (28), was collected as 3-phenylpentane and a fraction boiling at $78-81^{\circ}/6$ mm. weighing 13.0 g. (15%) was collected as 3-ethyl-3-phenylpentane.

3-Phenylpentane- d_9 (Procedure C)



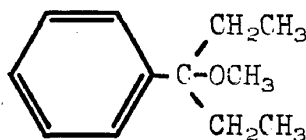
(a) Preparation of 3-phenyl-3-pentanol



Following the procedure described in the preparation of 2-phenyl-2-pentanol, ethyl magnesium bromide (prepared from 25 g. (1.04 moles) of magnesium turnings and 105 g. (0.96 mole) of ethyl bromide) was

treated with 67 g. (0.50 mole) of propiophenone. The 3-phenyl-3-pentanol produced was collected at $74^{\circ}/2.4$ mm., $n_D^{20} = 1.5152$, $n_D^{25} = 1.5126$ (literature value: b.p. $85-8^{\circ}/1$ mm., $n_D^{25} = 1.5128$) (35) and weighed 56.8 g. (70%).

(b) Preparation of 3-methoxy-3-phenylpentane.



In a manner similar to that described in the preparation of 2-methoxy-2-phenylbutane, 50.0 g. (0.31 mole) of 3-phenyl-3-pentanol, 120 ml. (3.0 moles) of methanol and 2.6 ml. of sulfuric acid were allowed to stand for three days. Upon distillation, 22.0 g. (41%) of 3-methoxy-3-phenylpentane, b.p. $74-5^{\circ}/3.5$ mm., $n_D^{20} = 1.5030$ was collected.

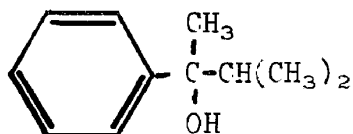
(c) Cleavage and hydrolysis of 3-methoxy-3-phenylpentane.

Using the procedure described under the preparation of cumene- d_5 , 18.4 g. (0.103 mole) of 3-methoxy-3-phenylpentane and 7.7 g. (0.20 mole) of potassium metal were permitted to react at 68° for eleven hours, after which 6.2 g. (0.31 mole) of deuterium oxide was added and the resulting 3-phenylpentane distilled. The fractions boiling at $67.5-68.5^{\circ}/10$ mm., $n_D^{20} = 1.4876$, weighed 8.3 g. (56%). Mass spectrometric analysis indicated: $d_1 = 53.3\%$, $d_0 = 46.7\%$, no beta- or gamma-deuterium atoms.

2-Methyl-3-phenylbutane

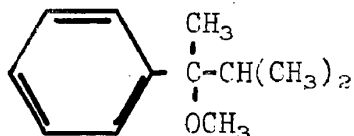
Attempts to prepare this compound by reduction of 2-methyl-3-phenyl-2-butene resulted in mixtures of the olefin and saturated hydrocarbon. The hydrocarbon was prepared using Procedure C, ordinary water being used instead of deuterium oxide in the hydrolysis step.

(a) Preparation of 3-methyl-2-phenyl-2-butanol.



This alcohol was prepared in a similar manner to that described for 2-phenyl-2-pentanol. To isopropyl magnesium chloride (formed from 75.0 g. (0.96 mole) of isopropyl chloride and 25.0 g. (1.03 moles) of magnesium turnings) was added 60 g. (0.50 mole) of acetophenone. The alcohol was obtained in 54% yield (44.3 g.), b.p. 76-7°/2.5 mm., $n_D^{20} = 1.5189$ (literature values: 77.0-77.5°/2.6-2.9 mm., $n_D^{25} = 1.5137$) (36).

(b) Preparation of 2-methoxy-3-methyl-2-phenylbutane.



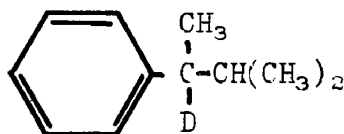
Following the procedure outlined in the preparation of 2-methoxy-2-phenylbutane, 39.6 g. (0.24 mole) of 3-methyl-2-phenylbutan-2-ol, 100 ml. (2.5 moles) of methanol and 2.5 ml. of sulfuric acid after

standing three days yielded 22.3 g. (52%) of 2-methoxy-3-methyl-2-phenylbutane, b.p. $72-5^{\circ}/4.0$ mm., $n_D^{20} = 1.4992$.

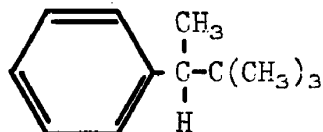
(c) Cleavage and hydrolysis of 2-methoxy-3-methyl-2-phenylbutane.

To 11.8 g. (0.30 mole) of potassium metal and 27.0 g. (0.15 mole) of 2-methoxy-3-methyl-2-phenylbutane in dry heptane (which had been allowed to react at 68° for six hours) was added 10 ml. of water in 75 ml. of tetrahydrofuran. Work-up gave 15.6 g. (71%) of 2-methyl-3-phenylbutane, b.p. $63^{\circ}/8.8$ mm., $n_D^{20} = 1.4912$ (literature values: b.p. $66.2^{\circ}/10$ mm., $n_D^{20} = 1.486$) (28).

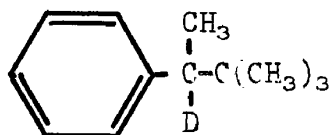
3-Methyl-2-phenylbutane- d_{α} (Procedure C)



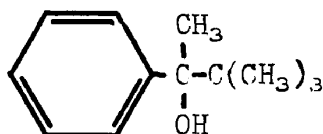
Using the procedure described in the preparation of cumene- d_{α} , 20.8 g. (0.12 mole) of 2-methoxy-3-methyl-2-phenylbutane and 8.3 g. (0.21 mole) of potassium metal were allowed to react for eight hours at 68° . Then 5.3 g. (0.26 mole) of deuterium oxide was added and the resulting 3-methyl-2-phenylbutane collected as those fractions boiling from $69.5-70.0^{\circ}/12$ mm., $n_D^{20} = 1.4903$. The yield was 12.1 g. (83%). Mass spectrometric analysis showed: $d_1 = 70.1\%$, $d_0 = 29.1\%$, no beta- or gamma-deuterium atoms.

2,2-Dimethyl-3-phenylbutane

This procedure is similar to that employed by Schmerling and West (37). A one-liter round-bottomed three-necked flask equipped with a stirrer, condenser, addition funnel and a dry argon inlet was thoroughly dried using a free flame. To the Grignard reagent from the iodine-initiated reaction of 20 g. (0.82 mole) of clean magnesium turnings with 92 g. (1.0 mole) of tert-butyl chloride in anhydrous ether was added dropwise at 0° a solution of 90 g. (0.50 mole) of α -phenethyl bromide (prepared in 81% yield from α -methylbenzyl alcohol and phosphorous tribromide) in 50 ml. of dry ether. Work-up as usual, using dilute hydrochloric acid for hydrolysis, gave 20 g. of product, b.p. 76-8°/9 mm., $n_D^{20} = 1.4973$. A higher boiling fraction (b.p. 130-160°/5 mm.) was also collected which crystallized upon cooling. Recrystallization from methanol gave white needles, m.p. 123-4°. This solid was believed to be 2,3-diphenylbutane (literature value: m.p. 126°) (38). The liquid fraction was refluxed over sodium metal for one hour, then fractionally distilled. Product boiling from 63-4°/5 mm., $d_4^{25} = 0.892$, $n_D^{20} = 1.4951$ (literature values: 50-1°/1 mm., $n_D^{20} = 1.4950$) (31), weighing 10.5 g. (13%) was collected as 2,2-dimethyl-3-phenylbutane.

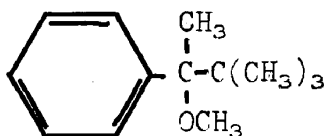
2,2-Dimethyl-3-phenylbutane-d₁ (Procedure C)

(a) Preparation of 3,3-dimethyl-2-phenylbutan-2-ol



The general method outlined for the preparation of 2-phenyl-2-pentanol was followed. To tert-butyl magnesium chloride (prepared from 180 g. (1.95 moles) of tert-butyl chloride and 50 g. (2.06 mole) of magnesium turnings) was added 125 g. (1.04 mole) of acetophenone. Distillation through a Vigreux column gave 97.4 g. of product boiling at 53-90°/1.2 mm. Redistillation through a packed column gave 41.2 g. (23%) of a product, b.p. 71°/1.2 mm., $n_D^{20} = 1.5164$.

(b) Preparation of 2-methoxy-3,3-dimethyl-2-phenylbutane.



An attempt to prepare this compound from 3,3-dimethyl-2-phenylbutan-2-ol and methanol resulted only in recovery of starting material. The ether was prepared, however, employing a method similar to that of Zeiss (32). In a dry one-liter three-necked round-bottomed flask

equipped with an addition funnel, condenser, dry argon inlet and high-speed stirrer was placed 400 ml. of anhydrous benzene and 36.4 g. (0.204 mole) of 3,3-dimethyl-2-phenylbutan-2-ol. Freshly-cut potassium metal (8.1 g.; 0.21 mole) was then added to the water-white solution. Reflux for three days was necessary for the red potassium salt to be produced. After this period 85.0 g. (0.60 mole) of methyl iodide was added and the mixture refluxed with stirring for twenty hours. After the sodium iodide was allowed to settle, the solution appeared almost colorless. Water (120 ml.) was added to the stirred mixture, the bottom aqueous layer separated and extracted with 200 ml. of ether, and the combined organic layers dried over 20 g. of anhydrous magnesium sulfate. Solvent was removed using a steam bath and the yellow residue fractionated, yielding 25.5 g. (78%) of 2-methoxy-3,3-dimethyl-2-phenylbutane, b.p. $79-84^{\circ}/3.3$ mm., $n_D^{20} = 1.5041-1.5065$.

(c) Cleavage and hydrolysis of 2-methoxy-3,3-dimethyl-2-phenylbutane.

Following the procedure described in the preparation of cumene- d_6 , 25.5 g. (0.133 mole) of 2-methoxy-3,3-dimethyl-2-phenylbutane and 10.3 g. (0.26 mole) of potassium metal were allowed to react for thirteen hours at 68° . Then 7.5 g. (0.38 mole) of deuterium oxide was added and the resulting 3,3-dimethyl-2-phenylbutane distilled. The fractions boiling from $64-6^{\circ}/4.6$ mm., $n_D^{20} = 1.4952$, and weighing 11.8 g. (55%) were combined. Mass spectrometric analysis gave $d_1 = 51.4\%$, $d_0 = 48.6\%$, no beta- or gamma-deuterium atoms.

High Surface Sodium (HSS)

Following the general procedure described in the bulletin "High Surface Sodium on Inert Solids" (39), 25 g. of dry Norite and 2.5 g. of freshly-cut sodium metal were stirred together at 160° for forty minutes and then allowed to cool to room temperature. The HSS was removed through a "goose-neck" with a 24/40 standard tapered joint at one end and a 14/35 joint at the other. The smaller joint was taped to small, previously weighed, sample vials and the larger joint was fitted to the reaction flask. By tilting the complete apparatus, the HSS could be made to enter the vials, approximately one gram being placed in each vial.

High Surface Potassium (HSP) was similarly prepared.

B. Exchange Studies

In principle, the procedure consisted in heating a mixture of an α -deuterated alkylaromatic and two non-deuterated alkylaromatics in the presence of an appropriate catalyst, withdrawing samples periodically, separating the structurally pure components and analyzing each for its deuterium content. A variety of conditions was studied before a suitable procedure was developed which gave satisfactory kinetic results.

Analytical Procedure

Because a mass spectrometer was not available for routine analyses, the deuterium content of the various hydrocarbons, after being subjected

to exchange conditions, was determined using the C-D stretching frequency in the infrared. Samples of all deuterated hydrocarbons were analyzed mass spectrometrically by Mr. S. Meyerson, Standard Oil Company (Indiana), Whiting, Indiana. The infrared spectra of solutions of these deuterated hydrocarbons in carbon tetrachloride were recorded using a Perkin-Elmer Model 21 double-beam infrared spectrophotometer with sodium chloride cells of 0.515 mm. width.

It was originally intended to use ethylbenzene- d_4 as the deuterium source and to compare the rate of self-exchange of ethylbenzene with the rate of exchange with another hydrocarbon. Although there are appreciable differences in the infrared spectra of the pure ordinary, mono- α , and di- α,α deuterated ethylbenzenes (see Figures 15 and 16), a suitable analytical method could not be worked out for mixtures of these three due to the overlapping of their C-D absorption peaks. A similar situation was encountered in the case of ordinary, mono- α and di- α,α diphenylmethane. Hence, it was decided to use ethylbenzene- d_4 merely as a source of deuterium and to allow two different hydrocarbons to compete for the deuterium in the ethylbenzene- d_4 .

Calibration curves were prepared correlating the deuterium content of the various hydrocarbons with the intensity of the C-D stretching frequency in the infrared region near 4.7 microns. Samples of known deuterium content were prepared by diluting the mass spectranalyzed deuterated samples with ordinary hydrocarbon. The solvent was carbon tetrachloride (Mallinckrodt "Analytical Reagent") purified (40) by refluxing over mercury metal for three hours and under a solution of

100 g. of sodium hydroxide in 350 ml. of water and 100 ml. of 95% ethanol for two hours, washing three times with water, once with dilute sulfuric acid and three times with water, drying over anhydrous calcium chloride and carefully distilling from phosphorus pentoxide through a twenty-four inch glass helices-packed column (the first 15% being discarded). Usually the volume ratio of hydrocarbon to carbon tetrachloride was 1:1.4. Under the exchange conditions employed, seldom did a hydrocarbon gain more than 15% deuterium. Thus, most calibration curves were prepared using samples containing from 0-15% deuterium.

The gears of the infrared instrument were set to spread the region of interest (3.0-6.0 microns) over a 30 cm. range. At 3.000 microns, with both cells filled with solvent and in place, the instrument was adjusted to the following specifications:

Slit width	990
Response	1
Per cent Transmission	95
Gain	5
Suppression	2
Filter	Auto
Speed	4
Slit controls	Auto
Scanning control	For

The spectrum of solvent versus solvent was recorded. The 0% transmission line was obtained by closing the sample beam window and recording the spectrum of solvent in only the reference beam (this also

coincided with the maximum absorption of the C-H peak at 3.2-3.5 μ). The spectra of solutions containing known and varying amounts of deuterated hydrocarbon were recorded and the ratio of the percent transmittance of the solvent to the percent transmittance of the sample (I_0/I) was determined. The logarithm of this ratio (optical density) was plotted against percent deuterium content to obtain a linear relationship from which the percent deuterium in unknown samples was determined. Table II gives a typical example showing quantities of hydrocarbons used in the preparation of a calibration curve.

The volume ratio of hydrocarbon/carbon tetrachloride of 1:1.4 was used for the calibration curves of all deuterated hydrocarbons except 2,2-dimethyl-3-phenylbutane, for which a ratio of 1.80:0.06 was used. Several factors entered into this choice of 1:1.4. Foremost, when a mixture was separated using the Vapor Fractometer, volumes of only slightly over 0.1 ml. were collected (especially when only a small center "cut" was made to insure ultra-clean separation). Since a volume of 0.20 ml. was required to fill the infrared cells, a volume of 0.100 ml. of hydrocarbon and 0.140 ml. of carbon tetrachloride (total volume 0.240 ml.) resulted in sufficient quantity to fill the cells and also produced intense spectra capable of discerning small percentages of deuterium. Table III gives the analytical data used in the preparation of the calibration curve (Figure 1) for sec-butylbenzene- d_9 . Other calibration curves were similarly prepared and are recorded in the appendix of the thesis (Figures 10-14).

TABLE II

PREPARATION OF sec-BUTYL BENZENE SAMPLES OF KNOWN, VARYING DEUTERIUM CONTENT
FOR THE CONSTRUCTION OF THE CALIBRATION CURVE

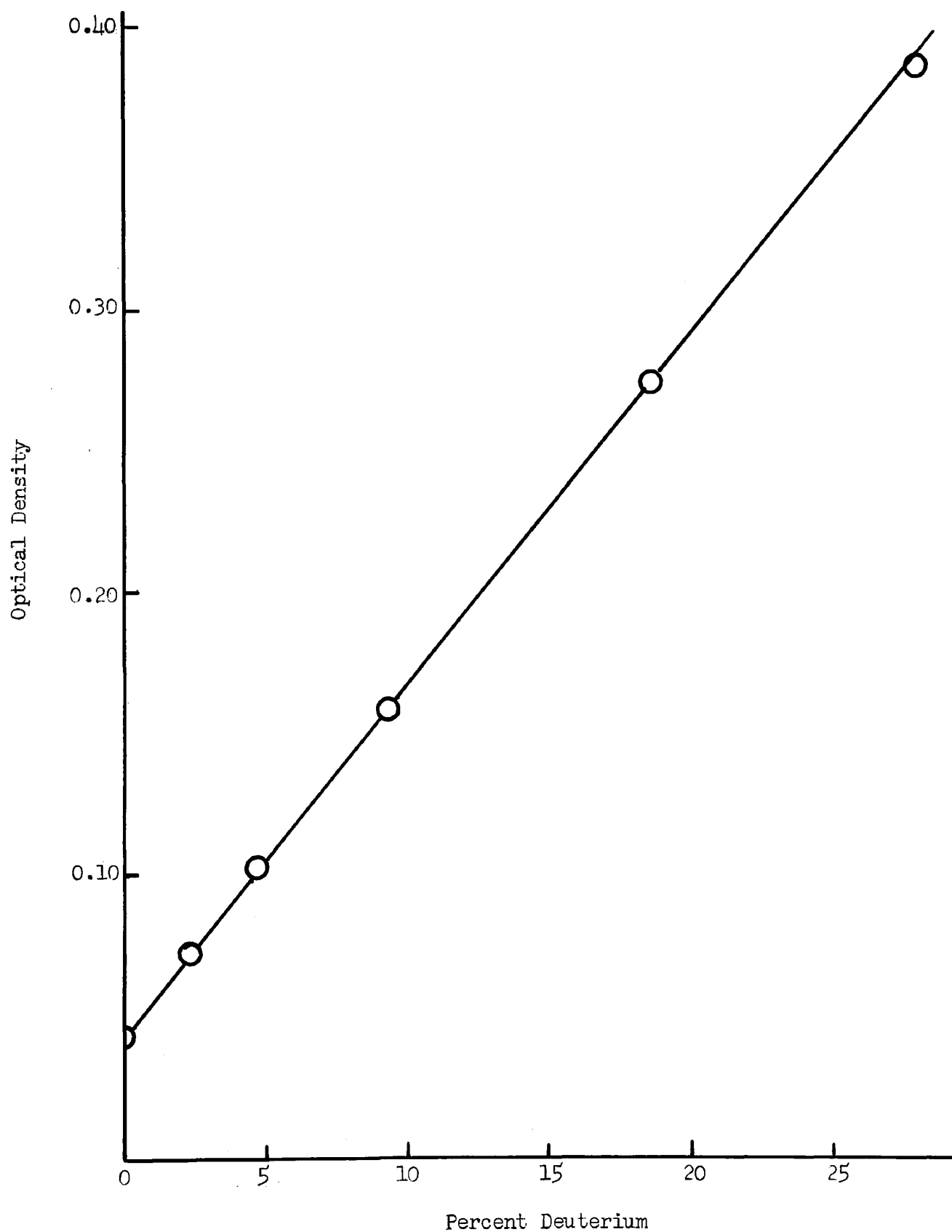
Sample	Percent D	s-butylbenzene Vol. (ML.)	s-butylbenzene-d ₆ (46.6%) Vol. (ML.)	Total Hydrocarbon Volume (ML.)	Solvent (CCl ₄) Vol. (ML.)
1	0.0	0.400	0.000	0.400	0.560
2	2.3	0.760	0.040	0.800	1.120
3	4.7	0.720	0.080	0.800	1.120
4	9.3	0.320	0.080	0.400	0.560
5	18.6	0.120	0.080	0.200	0.280
6	28.0	0.080	0.120	0.200	0.280

TABLE III

CALCULATION OF OPTICAL DENSITY FROM C-D BAND AT 4.68 MICRONS FOR
sec-BUTYLBENZENE (2.65 M) IN CARBON TETRACHLORIDE

Sample	Percent D	I_0/I	$D[\log (I_0/I)]$
1	0.0	1.105	0.0434
2	2.3	1.180	0.0719
3	4.7	1.267	0.1028
4	9.3	1.442	0.1590
5	18.6	1.885	0.2753
6	28.0	2.440	0.3874

Figure 1. Percent deuterium content of mixtures of sec-butylbenzene and sec-butylbenzene- d_9 in carbon tetrachloride vs. optical density at 4.68 microns. (Concentration of hydrocarbon = 2.65 M.)



Separation Procedure

Because of the expense of the deuterated compounds and unavailability of some of the ordinary hydrocarbons, only small quantities were used in the exchange reaction. Thus, it became necessary to develop a procedure for separating a three-component hydrocarbon mixture whose total volume was about one milliliter.

The first hydrocarbon chosen for exchange with ethylbenzene was diphenylmethane. It was felt that these might be separated using a chromatographic column. Although activated alumina proved unsuccessful, 80 mesh silica gel readily separated the two using carbon tetrachloride as the eluent. The progress of the hydrocarbons through the column was followed by taking the infrared spectrum of each 2-3 milliliter fraction as it was collected. However, this technique did not easily lend itself to the separation of hydrocarbons more closely related in structure, especially a three-component hydrocarbon mixture, so another method was sought for accomplishing this.

It appeared that gas chromatography was particularly attractive for separating such mixtures and, accordingly, a Perkin-Elmer Model 154 Vapor Fractometer was remodeled and adapted for this purpose. After considerable experimentation, best results were obtained using an asbestos-wrapped electrically-heated section of one-eighth inch copper tubing which extended six inches from the exit side of the instrument and to which was sealed a 10/30 standard tapered male joint. Only several seconds elapsed between the time a signal was recorded and the time the sample giving rise to that signal appeared at the exit.

The samples were collected in spiral traps whose dimensions are shown in Figure 2. The exit end of the spiral trap was protected with a drying tube containing Drierite. These traps, which were cooled in liquid air during the collection, proved quite efficient for gathering near-quantitative yields of the samples. Also, this method afforded a clean separation for the hydrocarbons used. The most difficult compounds to separate from each other were ethylbenzene and cumene, although even this was done with little difficulty as shown in Figure 3.

Originally, a two-meter one-fourth inch analytical column was used containing Perkin-Elmer packing type "A" (didecyl phthalate on firebrick). However, since this column was restricted to samples of about 0.05 ml., often five to six runs were necessary in order to collect a sufficient volume for quantitative infrared. This situation was remedied with the acquisition of a three-meter one-inch preparative column with packing of type "A" and a similar column of type "O" (silicone packing). These preparative columns permitted the clean separation of several milliliters of hydrocarbon mixture in from two to three hours. The carrier gas used with these larger columns was oil-pumped nitrogen and was usually regulated from 5-10 p.s.i. through the column.

The column temperature was operated near 100° until the ethylbenzene was collected, then often raised to 110-130° to hasten the passage of the remaining components. To insure a clean separation, from two to six minutes were allowed to elapse from the time a peak began to appear on the recorder until a trap was put in place to start the collection of that component. Likewise, the trap was removed several minutes

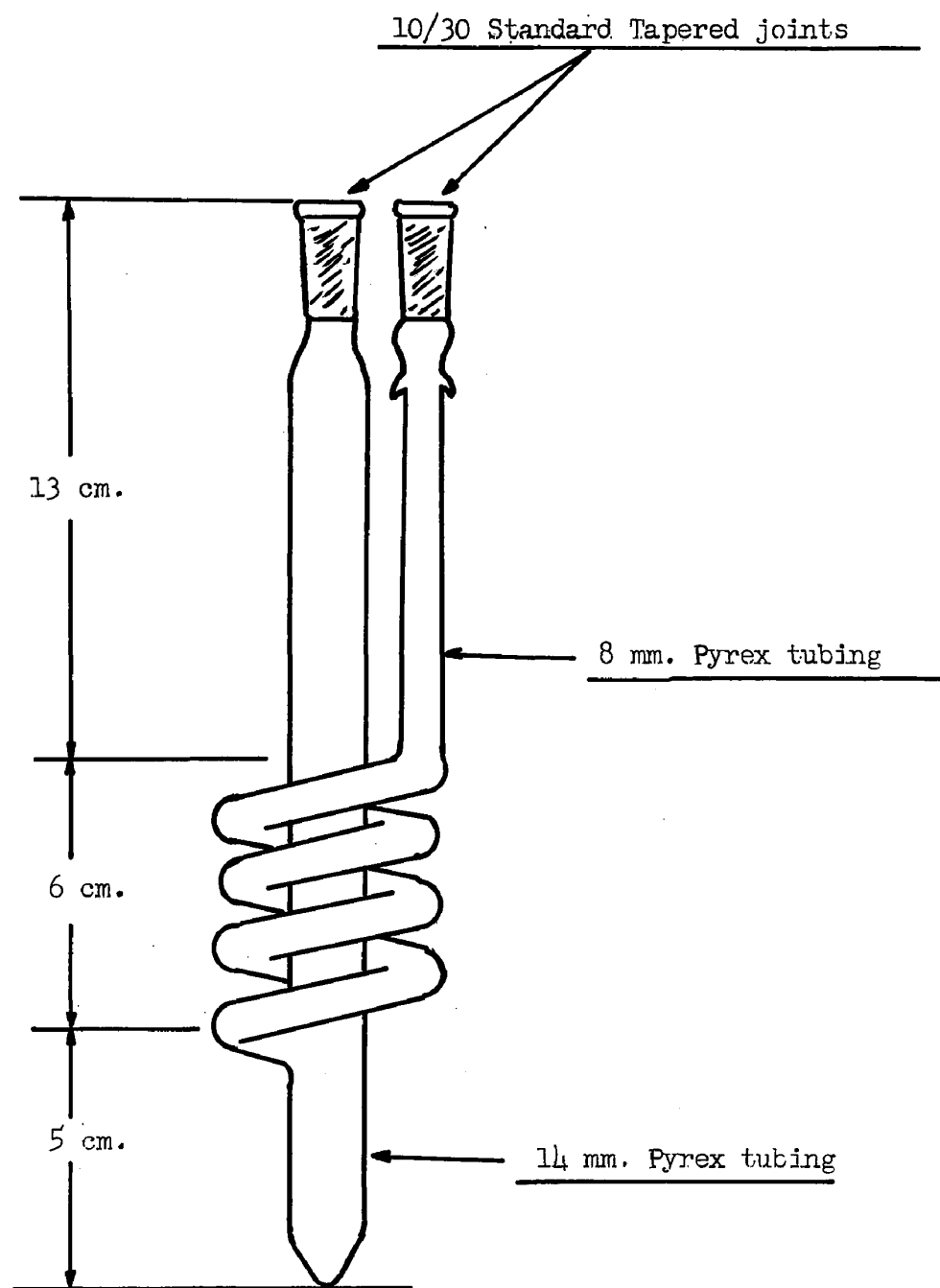


Figure 2. Spiral trap used with Vapor Fractometer for sample collection.

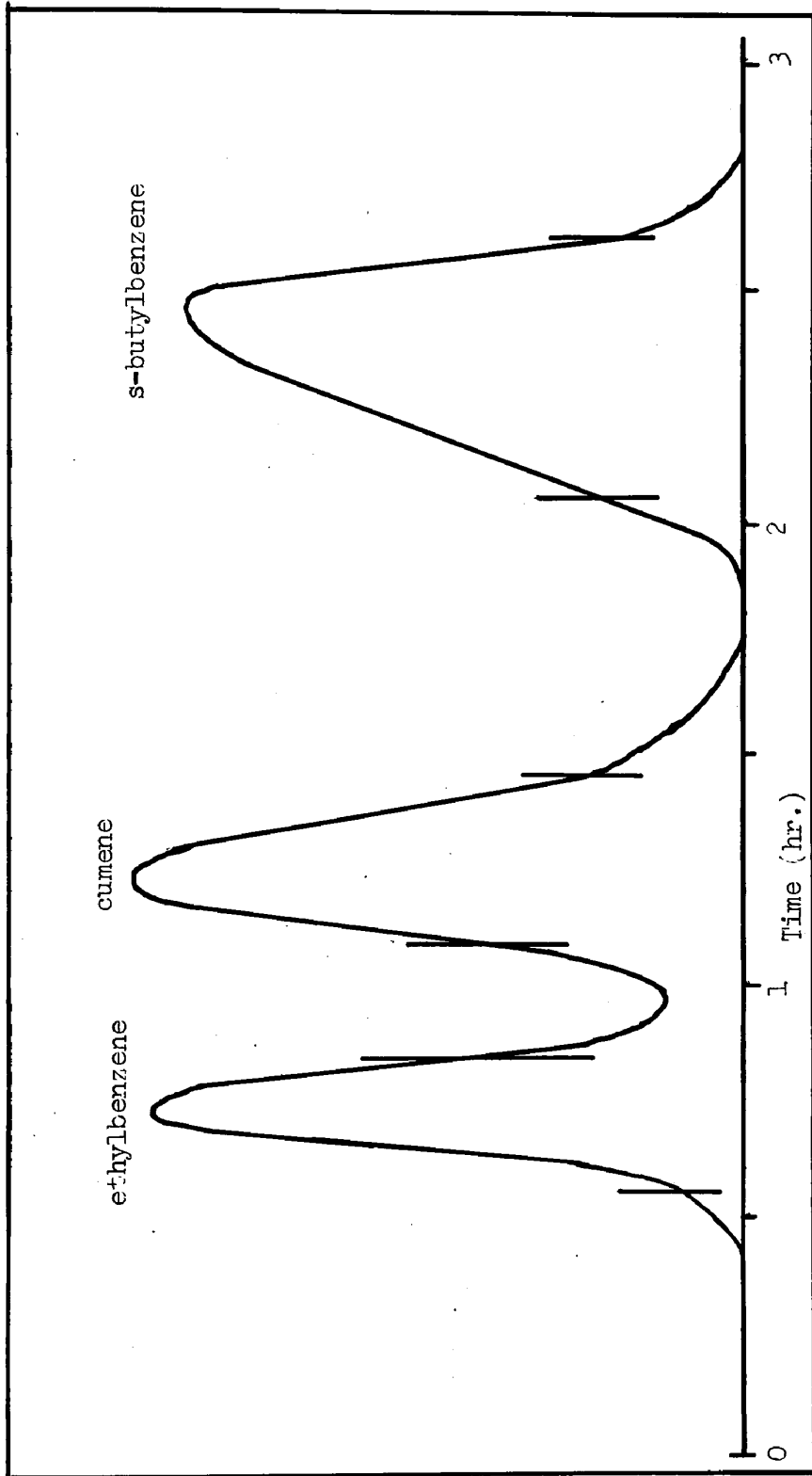


Figure 3. Gas chromatograph showing separation of ethylbenzene, cumene and sec-butylbenzene. (Column temperature, 94°; nitrogen pressure, 10 lbs.; vertical lines on peaks indicate when sampling for infrared analysis was started and stopped for each component.)

before the last of that hydrocarbon had passed through the detector. Further, the exit tube was rinsed with acetone and wiped clean before each trap was secured in place. As a trap was removed, a 10/30 male standard tapered plug was quickly inserted in the entrance end of the trap and, with the drying tube still on the exit end, the trap was allowed to reach room temperature (hastened by warming in a stream of water). Then the drying tube was removed and another plug inserted in its place.

After the liquid had drained to the bottom of the trap, the desired volume (usually 0.100 ml.) of compound was withdrawn using a 0.2 ml. pipette graduated to 0.005 ml., the appropriate amount (usually 0.140 ml.) of purified carbon tetrachloride added, the infrared spectrum of the mixture recorded and the percent deuterium determined using the calibration curve prepared for that hydrocarbon.

Exchange Experiments

(a) Apparatus

An autoclave of the type used in previous exchange reactions (17) did not readily lend itself to the sampling necessary for kinetic measurements nor did the temperature control seem adequate. Accordingly, several catalysts, temperatures and apparatus designs were studied with the hope of finding not only a more suitable reaction vessel, but optimum reaction conditions.

The vessel first used consisted of a 50-ml. Erlenmeyer flask with a 20-cm. West condenser sealed to the top of the flask. The catalyst and hydrocarbon components were added through the top of the condenser

which was fitted with a 19/38 female standard tapered joint. After the addition of the reactants, a male 19/38 standard tapered joint to which a stopcock was attached was placed in the top of the condenser.

Periodically, samples were removed from the flask through a heavy walled capillary tubing which entered the side of the Erlenmeyer through a ring seal. One end of the tubing extended to within an eighth inch of the bottom of the flask, while the other end led to a three-way stopcock. By the proper manipulation of this stopcock, the vessel could be flushed with a stream of dry argon before or during a run, the flask could be evacuated, or a sample could be withdrawn. Temperature was regulated by placing the flask in a constant temperature bath three inches deep, underneath which was a Mag-Mix magnetic stirrer for agitation.

In the course of this work, one hundred and nine exchange reactions were attempted, the first thirty being done in the apparatus described above. Appropriate catalysts, temperature ranges and hydrocarbons suitable for kinetic experiments were determined in this apparatus. Unfortunately, this reaction vessel suffered from several disadvantages for accurate kinetic measurements. These included frequent plugging of the capillary tubing with catalyst and the limitation that temperatures above the boiling point of any of the components often resulted in the condensation of that compound in the condenser thus reducing the possibility of exchange with that hydrocarbon.

Because of these difficulties, it was necessary to resort to sealed tubes for the kinetic experiments. Accordingly, segments of 15 mm.

Pyrex tubing eight inches long sealed at one end and with a neck approximately 8 mm. O.D. five inches from the sealed end were prepared. The tubes were dried at 110° for several hours before use. They were then attached to the end of a train which could supply dry argon (concentrated sulfuric acid, potassium hydroxide pellets) or a vacuum, with suitable stopcocks and mercury safety valve. The tube was successively evacuated and filled with argon approximately twenty times to insure removal of water vapor and oxygen. After a final filling with dry argon, the tube was removed and temporarily stoppered. The appropriate amount of hydrocarbon mixture was pipetted into the tube followed by the addition of a previously weighed quantity of catalyst. Usually it was necessary to cut the catalyst into several pieces so that it could easily pass through the constriction in the tube. For the occasional piece that did get stuck in the neck, a brass rod was used to push the catalyst into the main body of the tube. The tube was returned to the argon train, a slight vacuum applied and the tube sealed off at the constriction.

Temperature was controlled within $\pm 0.5^{\circ}$ using an insulated mineral oil bath one foot in diameter and one foot deep equipped with two 250-watt knife heaters and a bimetallic spiral regulator. Thorough, continuous mixing was accomplished by mounting the tubes on extension clamps which were attached to one arm of a Model BB, Burrell "Wrist-Action" Shaker (Burrell Corporation, Pittsburgh, Pennsylvania). The tubes were fixed at right angles to the arms of the shaker and the center of each tube moved in an arc approximately three inches long and alternated

direction over one hundred times every twenty seconds. The use of these sealed tubes proved very successful and all quantitative results were obtained using these as reaction vessels.

(b) Reaction Conditions

Several catalysts were investigated. A very reactive catalyst was desirable for allowing kinetics to be measured at low temperatures. High surface sodium (HSS) on charcoal and high surface potassium (HSP) on the same support were tried. It was found that exchange occurred with HSP as low as 65° , but unfortunately neither of these catalysts was very discriminating, appreciable deuterium occurring on the aromatic ring as well as the side chain as shown by the appearance of infrared bands at 4.40 microns (the aliphatic C-D band appears near 4.68 microns) (See Figure 4). The catalyst which was best suited for side-chain exchange proved to be potassium metal which, aside from being more easily handled than HSS or HSP, is a liquid above 63° , allowing a fresh surface of catalyst to be continually exposed to hydrocarbon during exchange. So that reproducible results could be obtained, samples of potassium had to be used which did not differ from one another in weight. It was found convenient to weigh the samples on a magnetically-damped chainomatic analytical balance. A weighing bottle two-thirds full of potassium metal-dried mineral oil was weighed to the nearest milligram. Then a piece of potassium roughly the weight desired was freshly cut under dry heptane, picked up with forceps, dried with absorbant paper, placed in the mineral oil in the weighing bottle and the bottle reweighed.

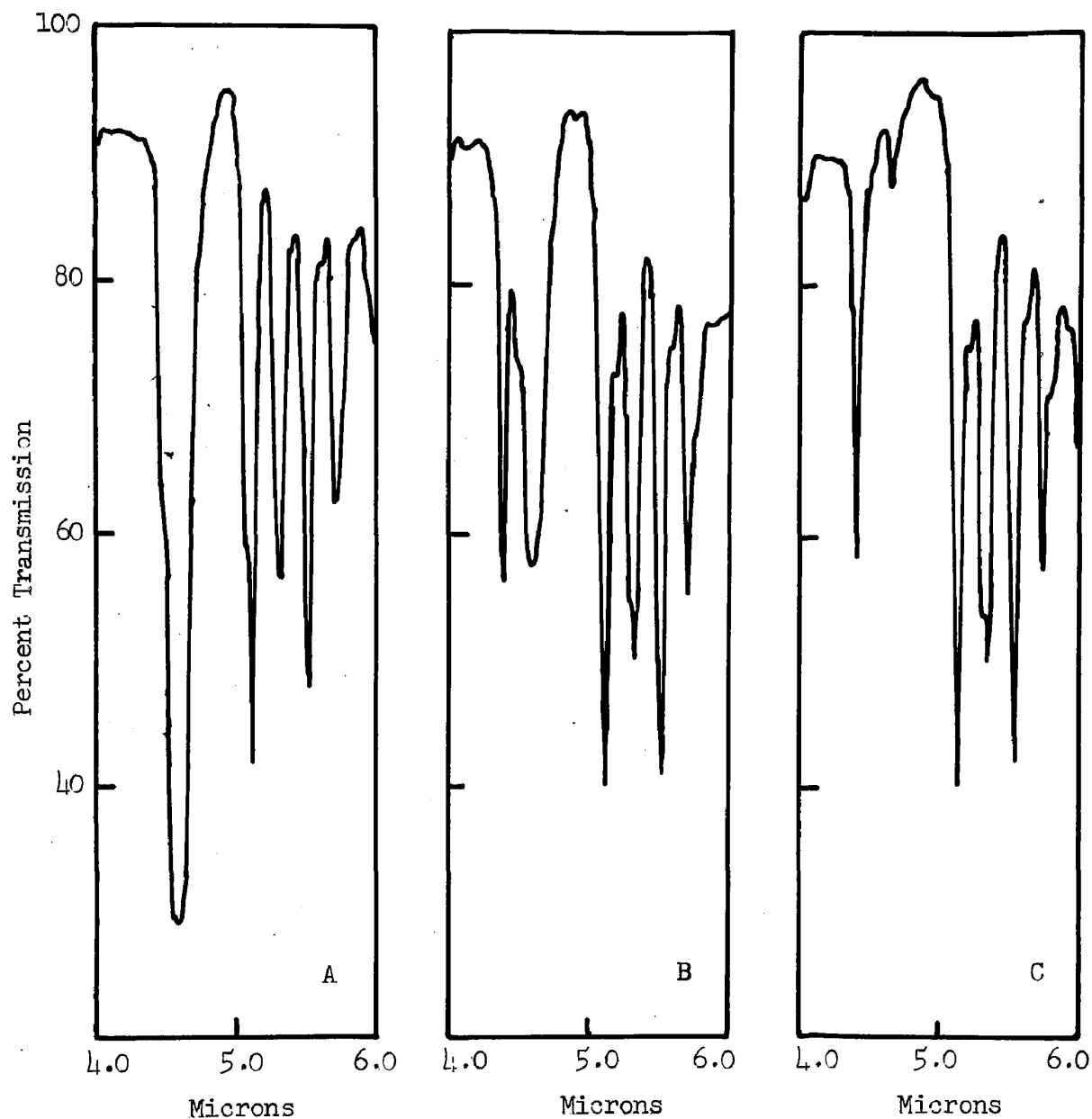


Figure 4. Ring exchange over high surface sodium (HSS) on charcoal.

A = Ethylbenzene-d₈

B = Ethylbenzene-d₈ after exchange with cumene at 100° for 6 hours over HSS.

C = Cumene after exchange with ethylbenzene-d₈ at 100° for 6 hours over HSS.

Note the appearance of two C-D bonds: aromatic C-D at 4.40 μ and aliphatic C-D at 4.68 μ .

This process of cutting and reweighing was repeated until the desired weight of catalyst was obtained. When it became necessary to cut the potassium into several pieces to make addition to the reaction tube easier, this cutting was likewise done under dry heptane, the metal being touched dry with absorbant paper before being placed in the tube.

Another factor which was studied was the effect of temperature. Experiments were run using the various catalysts from 65-175°. In all cases higher temperatures resulted in an increased rate of deuterium exchange, but, unfortunately, the rate of aromatic ring exchange increased more rapidly than the rate of side chain exchange. The temperature of 150° was finally selected as a suitable temperature for conducting the kinetics using potassium metal as a catalyst because the side chain exchange occurred at a desirable rate while the aromatic ring exchange was small.

(c) Kinetic Procedure

For each kinetic run a stock solution containing the proper ratio of hydrocarbon components was prepared. With the aid of a 1 ml. pipette graduated to 0.01 ml., identical volumes were placed in each tube from this stock solution. Most of the kinetics were done by preparing ten tubes and allowing two tubes each to react at 150° for two, four, six, eight and ten hours. At the designated time, each tube was quickly removed from the bath, cooled for a minute in a beaker of mineral oil at room temperature, then cooled in an ice bath. After several minutes the tube, which was usually covered inside with the deep-red color characteristic of the organometallic formed, was opened and the deep-red

liquid removed using a medicine dropper pulled to a capillary and added to 1 ml. of distilled water in a 30-ml. separatory funnel. There was some reaction when this was done, although usually no more than a gentle evolution of hydrogen. When this evolution had subsided (hastened by swirling the funnel), the bottom yellow, aqueous layer was withdrawn and the white hydrocarbon layer washed with another ml. of water. After removal of this aqueous phase, the remaining clear, colorless organic layer was withdrawn through the top of the funnel with a capillary medicine dropper and placed, together with several pieces of Drierite, in a test-tube three inches long constructed from 8 mm. Pyrex tubing. The tube was stoppered with a rubber serum bottle cap and labelled. The purpose of the serum bottle cap was the ease with which one could withdraw the sample into a hypodermic syringe and inject it into the Vapor Fractometer for separation.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

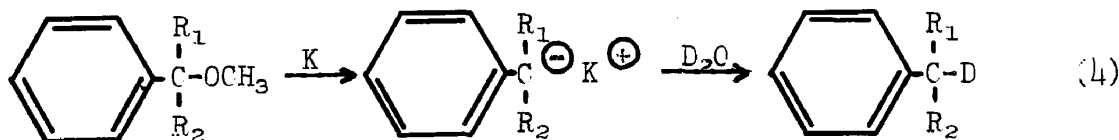
Synthetic Methods

Ordinary hydrocarbons which were needed for the exchange experiments were either obtained commercially or synthesized by methods reported in the literature. Samples of alpha-deuterated hydrocarbons of known deuterium content were also necessary for preparing calibration curves (correlating percent deuterium with the intensity of the C-D peak in the infrared) so that the amount of deuterium exchanged could be determined.

When it became apparent that synthesis by reduction of the appropriate tertiary chloride with lithium aluminum deuteride and lithium deuteride



resulted in poor yields of the desired compound, another route was sought. A method which appeared to be suited for this purpose was cleavage of the corresponding α -methyl ethers with an alkali metal (to form the organometallic compound) followed by hydrolysis with deuterium oxide.

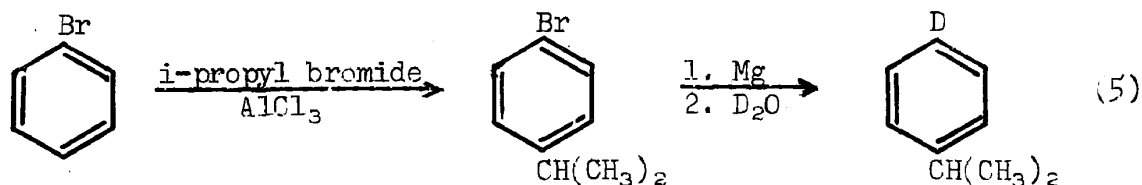


This procedure proved to be applicable for all the required compounds (see Table IV).

During the preparation of cumene- d_α by this procedure, a paper appeared by Russell (42) who claimed that cumene prepared in a similar manner (major differences were sodium-potassium alloy instead of potassium only, ether solvent rather than heptane and deuterium chloride instead of deuterium oxide to introduce the deuterium) contained 0.24 aromatic deuterium atoms per molecule. He analyzed the cumene by high resolution nuclear magnetic resonance, infrared and mass spectroscopy. It therefore became necessary to establish the position of the deuterium in the deuterated cumene prepared by the method described in this thesis (Mass spectrometric analysis of fragmentation peaks unfortunately does not allow one to distinguish ring- from alpha-deuterium (43)).

Proof of Structure of Cumene- d_α

The infrared spectrum of our product showed essentially no aromatic C-D band (4.4 microns), but the spectrum of Russell's product also showed only slight aromatic C-D absorption. In order to examine this band more carefully, cumene- d_p was prepared by the following scheme:



This product showed a strong aromatic C-D band at 4.40 microns (see Figure 20). The percentage of deuterium in the cumene- d_α and cumene- d_p

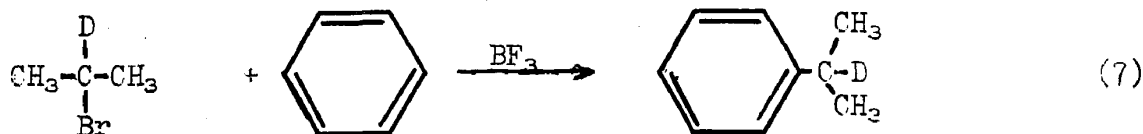
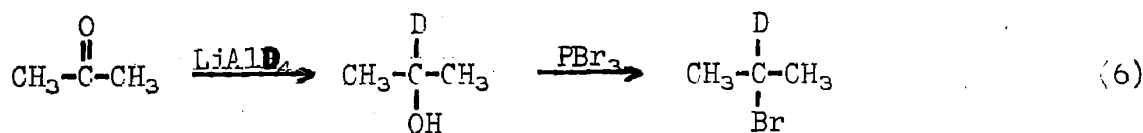
TABLE IV

YIELDS AND DEUTERIUM ANALYSES OF HYDROCARBONS PREPARED BY ETHER
 CLEAVAGE WITH POTASSIUM FOLLOWED BY HYDROLYSIS
 WITH DEUTERIUM OXIDE

Hydrocarbon	Yield From Ether (Percent)	Mass Spectrometric Analysis	
		Percent d ₁	Percent d _o
Cumene	57	82.6	17.4
sec-Butylbenzene	64	46.6	53.4
2-Phenylpentane	64	64.1	35.9
3-Phenylpentane	56	53.3	46.7
2-Methyl-3-phenylbutane	83	70.1	29.9
2,2-dimethyl-3-phenylbutane	55	51.4	48.6

Note: Mass spectrometric analyses are within 1% of absolute value and show no beta, gamma or delta deuterium atoms.

were essentially identical (82.6% and 82.7% respectively). Aromatic deuterium was easily discernable in mixtures containing a 1:9 and 1:4 ratio of cumene-d_p to cumene-d_α (see Figure 5). It is safe to conclude, therefore, that according to infrared analysis, cumene-d_α prepared by ether cleavage as described in this thesis contained < 5% aromatic deuterium. Furthermore, a sample of cumene-d_α prepared by the following scheme



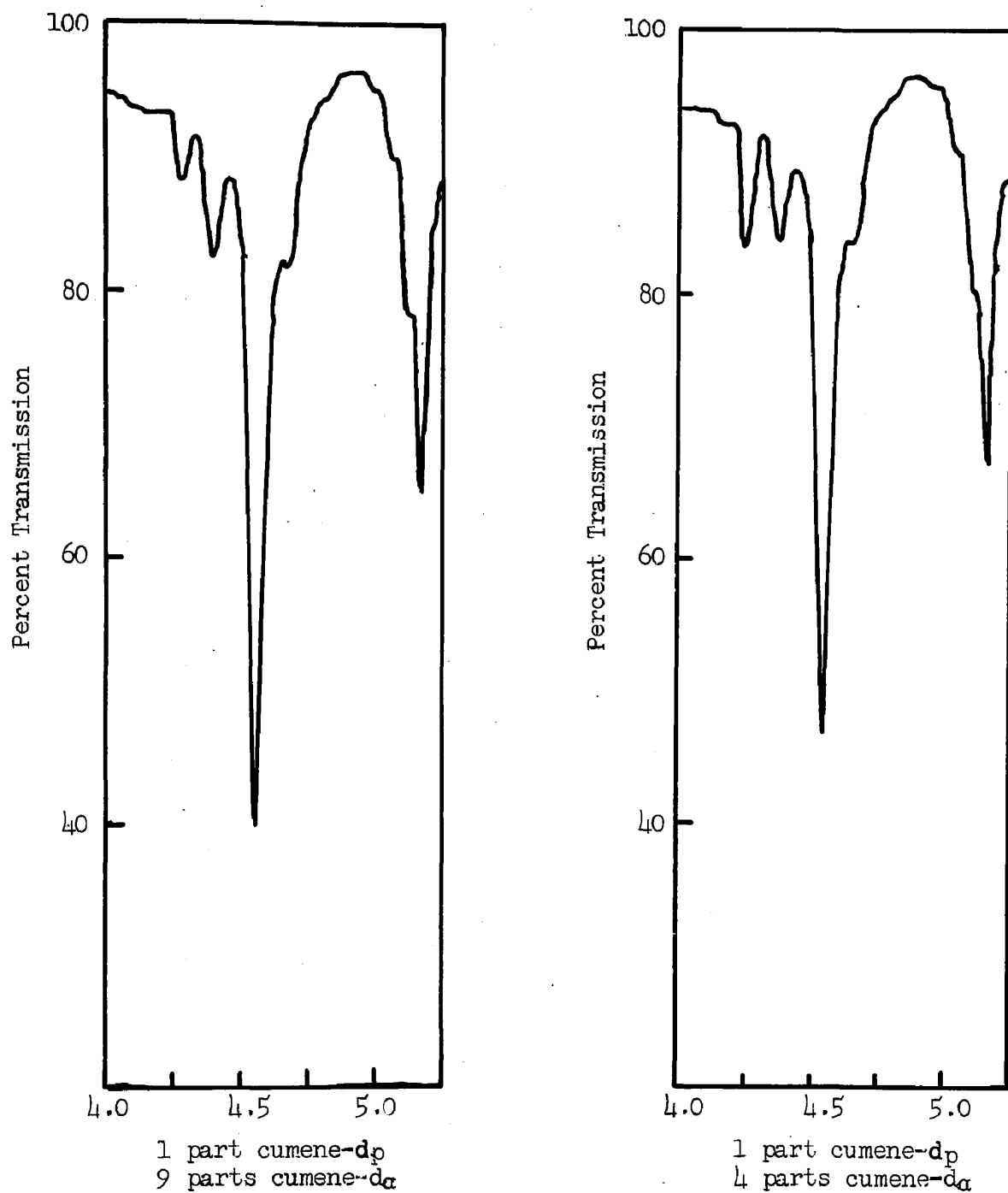


Figure 5. Infrared spectra showing relative absorption due to a 1:9 and 1:4 ratio of cumene- d_p in cumene- d_α . The aromatic C-D band (4.40 microns) roughly doubles in intensity, indicating the absence of ring-deuterated material in the cumene- d_α prepared by ether cleavage.

(and kindly supplied by A. Streitwieser, Jr.) had an infrared spectrum essentially identical with that of the cumene- d_α prepared in this laboratory.

The nuclear magnetic resonance spectra (see Figure 6) are also consistent with the structural assignments based on infrared. The C band (due to methyl protons on the side chain) is split in ordinary, ring-deuterated and p-bromocumene, but not in the product from ether cleavage. This splitting is due to the α -proton in the first three compounds and, therefore, only a low (< 20%) percentage of the α -hydrogens in the product from ether cleavage can be protons; the rest must be deuterons. Furthermore, a B band, due to the tertiary proton of the side chain, is totally absent from this material, whereas it appears in the other three spectra.

Finally, cumene- d_α (from ether cleavage) and cumene- d_p were oxidized to benzoic acid. Unfortunately, the region in the benzoic acid spectrum from 4.4-4.8 microns is not free from interferences. A strong band at 4.40 microns attributable to aromatic C-D was observed, however, in the benzoic acid obtained from cumene- d_p . From the spectra of mixtures, one can conclude that there is less than eight percent ring deuteration in the cumene- d_α .

A sample of cumene- d_α (prepared by ether cleavage and addition of deuterium oxide) was sent to Russell who agreed that it contained little or no aromatic deuterium. (For an explanation of the difference in behavior of deuterium chloride in ether vs. deuterium oxide, see reference 57.)

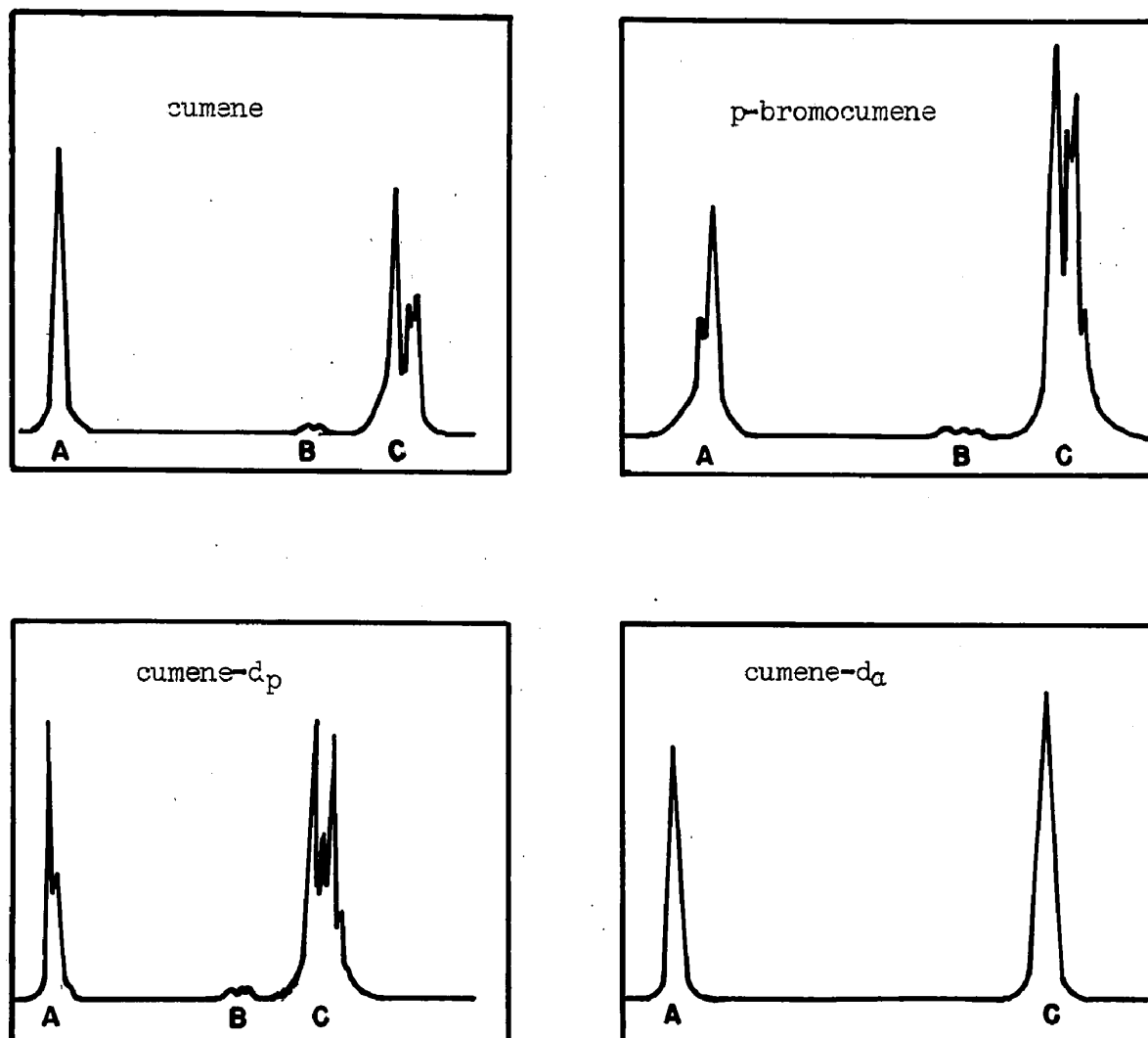
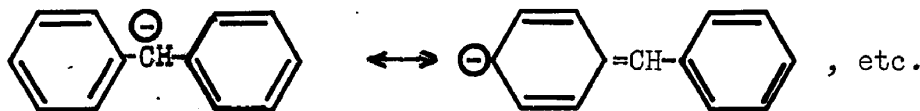


Figure 6. Nuclear magnetic resonance spectra of various cumenes. The lack of splitting of the C band and the total absence of a B band in the spectrum of cumene-d_a are results entirely consistent with the structural assignment. The A band is due to protons on the aromatic ring.

Preliminary Exchange Experiments

Initial experiments were with ethylbenzene- d_α and diphenylmethane, it being thought best to look for large differences in acidity first. No exchange occurred under the conditions employed, which included temperatures from 80-175°, reaction times from 2-67 hours and the use of potassium metal, high surface potassium (HSP) and high surface sodium (HSS) as catalysts. This unanticipated result was apparently caused by too great a difference in acidity. The diphenylmethyl anion, resonance stabilized by two aromatic rings, presumably was not sufficiently basic to remove a deuteron from ethylbenzene.



The next exchange attempts were between ethylbenzene- d_α and cumene whose acidities were expected to be more comparable. Here also, potassium metal, HSP and HSS were used as catalysts. Appreciable exchange occurred in each case, both in the stirred reactor and in sealed tubes. Unfortunately, the self exchange of ethylbenzene- d_α is difficult to analyze quantitatively with infrared. It was decided therefore to restrict the study to hydrocarbons containing only one benzylic (alpha) hydrogen and to allow two non-deuterated hydrocarbons to compete for the deuterium in a third. Because of the extensive deuterium exchange with the aromatic ring when HSS and HSP were used (see Figure 4), potassium metal was used as the exchange catalyst in all additional experiments. Further, because of the reasons listed in

the Experimental section, use of the reaction flask was discontinued and sealed tubes used in all subsequent reactions.

The competition between cumene and sec-butylbenzene for the deuterium in ethylbenzene- d_α , using potassium metal as catalyst, was extensively studied. It was found that while ring exchange at 130-140° was only slight, the rate of side chain deuteration was also retarded compared to higher temperatures. Most kinetics were therefore carried out at 150°, a temperature which gave measurable exchange rates in reasonable times (ten hours) but still was sufficiently low to make ring deuteration a minor side reaction.

The effect of using ethylbenzene- d_α compared with cumene- d_α as a source of deuterium was studied. Reactions in which sec-butylbenzene competed with 2-methyl-3-phenylbutane using ethylbenzene- d_α in one case and cumene- d_α in the other were run using identical temperatures and amounts of catalyst. It was found that more ring deuteration occurred with cumene- d_α than with ethylbenzene- d_α . Also, side-chain deuteration proceeded 30-50% farther with ethylbenzene- d_α than with cumene- d_α (see Figure 7). These results might have been anticipated because the inductive effect of the additional methyl group in cumene would make its alpha hydrogen less acidic than those in ethylbenzene. This means that an alpha-deuterium atom in ethylbenzene, being more labile, would be more readily exchanged than one in cumene. The fact that exchanges using cumene- d_α result in more ring deuteration in the competing hydrocarbons is probably likewise related to the decreased acidity. Bryce-Smith (5), who studied the metallation reaction between cumene

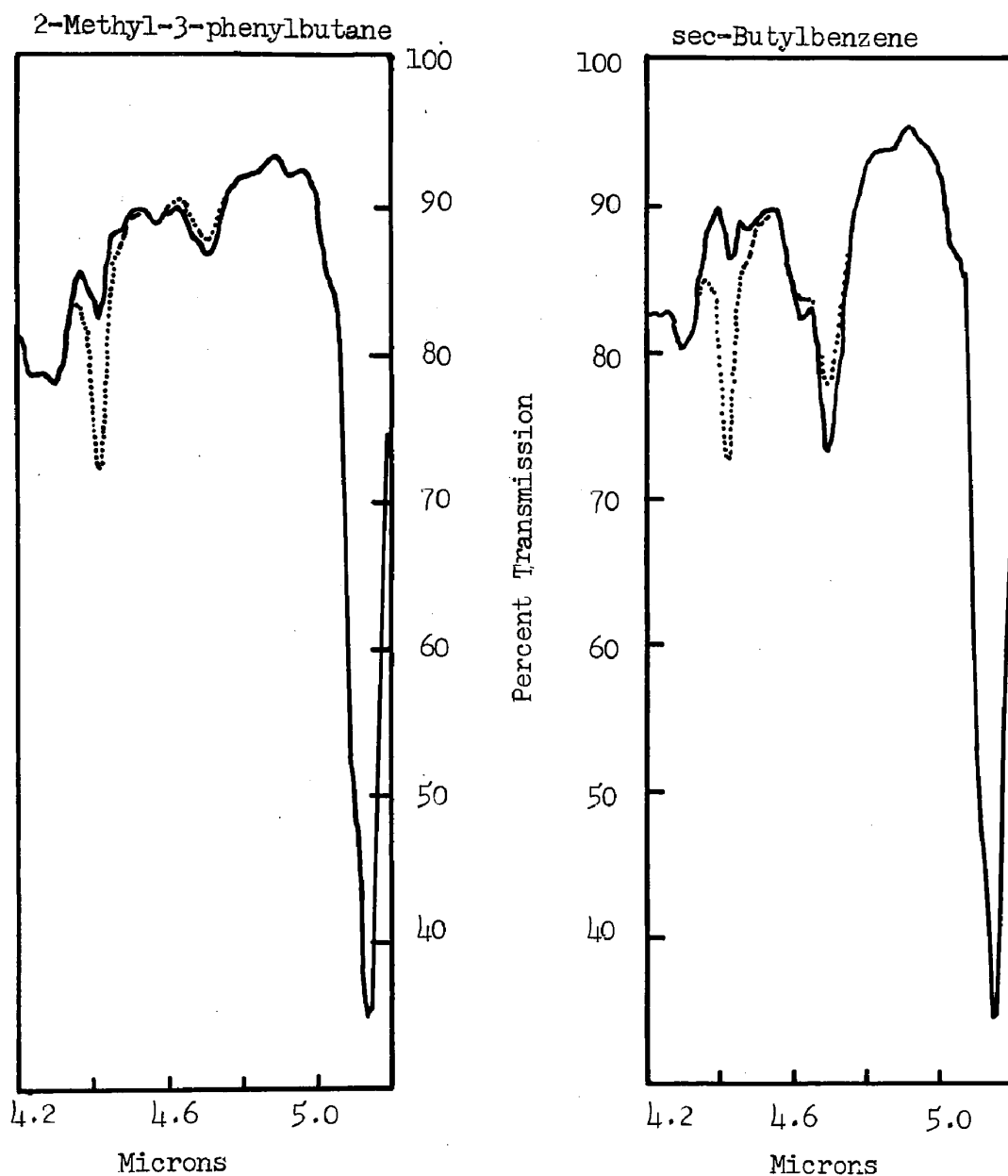
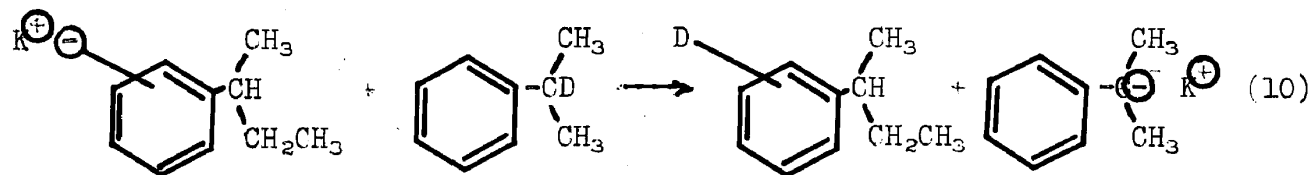
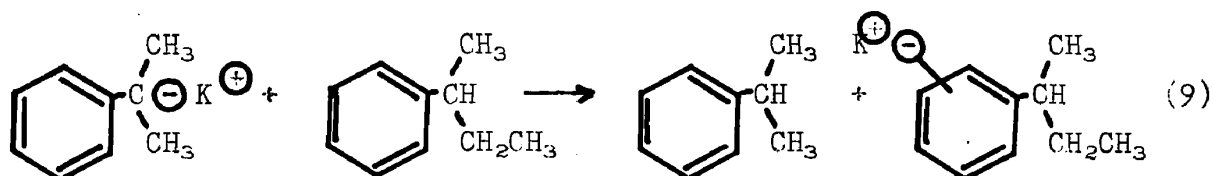
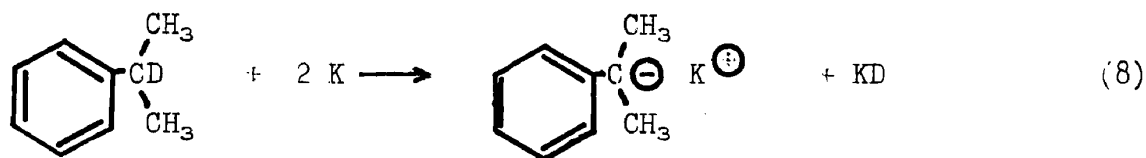


Figure 7. Infrared spectra illustrating the dependence of exchange on the deuterium source. sec-Butylbenzene and 2-methyl-3-phenylbutane were allowed to compete for the deuterium in ethylbenzene-d₉ (solid line) and cumene-d₉ (dotted line). Exchanges with cumene-d₉ resulted in more deuterium in the ring (4.40 microns) and less in the side chain (4.68 microns).

and ethylpotassium, found the para and meta hydrogens in cumene to be more easily removed than the alpha. He interpreted this as meaning that these ring positions were more acidic. Correspondingly, the dimethylphenyl carbanion formed from cumene, being more basic than the corresponding ion from ethylbenzene, might easily extract an aromatic hydrogen from sec-butylbenzene or 2-methyl-3-phenylbutane. The resulting carbanion could attack another molecule of cumene-d_α to form the product with ring deuterium. This sequence of reactions is shown below.

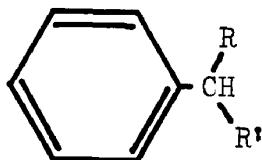


For the kinetic experiments, then, ethylbenzene-d_α was used as the source of exchangeable deuterium.

Kinetic Experiments

Kinetics were followed by allowing exchange reactions to run in sealed tubes for various periods of time, then analyzing for the percent deuterium in the originally non-deuterated components using quantitative infrared.

The hydrocarbons studied corresponded to



where the alkyl groups were:

<u>R</u>	<u>R'</u>
CH ₃	CH ₃
CH ₃	C ₂ H ₅
CH ₃	n-C ₃ H ₇
CH ₃	i-C ₃ H ₇
CH ₃	t-C ₄ H ₉
C ₂ H ₅	C ₂ H ₅

In one experiment, phenylcyclopropane was examined in competition with cumene for the deuterium in ethylbenzene-d_α. After 8-10 hours over potassium at 150°, the cumene had exchanged as expected (12.9%-d_α after 10 hours), but the phenylcyclopropane could not be recovered; it apparently polymerized as evidenced by a loss in liquid volume and the production of considerable black, tarry residue. Although phenylcyclopropane does not appear amenable to study by this method, it is possible that phenylcycloalkanes with larger rings could be so studied.

It was desirable to demonstrate that no rearrangements or other side reactions occurred during an exchange run. After the quantitative infrared spectra of the reactants from the sample of maximum reaction time were recorded, these solutions were diluted from the 1:1.4 volume ratio to a 1:20 ratio of hydrocarbon to carbon tetrachloride and the infrared spectra examined from 2.0-14.5 microns. These were compared

with the spectra of the ordinary hydrocarbons. In no case was any change noted other than those caused by the substitution of deuterium in the molecule. Also, a "blank" run was carried out between sec-butylbenzene and 2,2-dimethyl-3-phenylbutane using potassium metal and ordinary ethylbenzene. The infrared spectra of both the sec-butylbenzene and the 2,2-dimethyl-3-phenylbutane after exchange were identical with those before exchange.

The amount of catalyst and the concentration of the reactants affected the absolute rates of exchange. The usual quantities used in each sealed tube were: 0.0051 mole (0.20 g.) of potassium metal, 0.00286 mole of each ordinary hydrocarbon and from 0.350 ml. (0.00285 mole) to 0.600 ml. (0.00493 mole) of ethylbenzene- d_4 . As might be anticipated, the rate of exchange was not as great when a smaller molar ratio of catalyst was used, although the relative rates were still similar (see Table V). Further, it was discovered that altering the molar ratio of the two competing hydrocarbons resulted in a decrease in the percent deuterium exchanged, although the total number of moles of deuterium exchanged remained approximately constant (see Table VI).

Within a given exchange run, the weight of potassium metal in each sample varied no more than 2-3% and the volumes of hydrocarbon were within 1-2% of each other. The precision to which the quantitative infrared could be interpreted was $\pm 0.2\%$ deuterium.

Table VII lists the results of a kinetic run involving competition between cumene and sec-butylbenzene. The remaining kinetic runs are given in the Appendix. Figure 8 shows the progressive appearance of the C-D peak during this exchange.

TABLE V

EFFECT OF CATALYST QUANTITY ON THE RATES OF EXCHANGE OF CUMENE AND *sec*-BUTYL BENZENE
(Ethylbenzene- d_6 is deuterium source, $T = 150^\circ$)

Compound	Weight of Potassium (g.)	Rates $k \times 10^6 (\text{sec}^{-1})$	Relative Rates	
			(cumene/ <i>sec</i> -butylbenzene)	$\frac{k_{0.1 \text{ g.}}}{k_{0.2 \text{ g.}}} \times 100$
cumene	0.2	5.64		74.7
	0.1	4.21		
<i>sec</i> -butylbenzene	0.2	2.43		74.9
	0.1	1.82		
	0.2		2.32	
	0.1		2.32	

TABLE VI

EFFECT OF CONCENTRATIONS ON RATES OF EXCHANGE
(T = 150°, time = 4 hours)

Sample	Volume (ml.)			Percent D		Total Deuterium Exchanged
	Ethylbenzene-d ₅	Cumene	s-Butylbenzene	Cumene	s-Butylbenzene	
1	0.350	0.400	0.445	8.2	3.9	12.1
2	0.350	0.400	0.890	5.9	2.7	11.3

TABLE VII.

COMPETITION BETWEEN CUMENE AND sec-BUTYLBENZENE
(0.20 g. potassium metal, 150°, 1.200 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Wt. (g.)	Percent Deuterium Exchanged	
			Cumene	sec-Butylbenzene
1	2	0.204	3.0	1.6
2 [†]	2	0.203	2.5	1.9
3	4	0.200	7.0	2.6
4 [†]	4	0.203	8.2	3.9
5	6	0.204	12.2	5.8
6 [†]	6	0.199	11.2	4.3
7	8	0.202	15.4	7.5
8 [†]	8	0.196	16.5	7.2
9	10	0.196	18.7	8.3
10 [†]	10	0.196	16.8	8.2

*Stock solution: 3.680 ml. ethylbenzene-d₅; 4.200 ml. cumene; 4.680 ml. sec-butylbenzene.

[†]These points were determined two weeks after the odd-numbered samples.

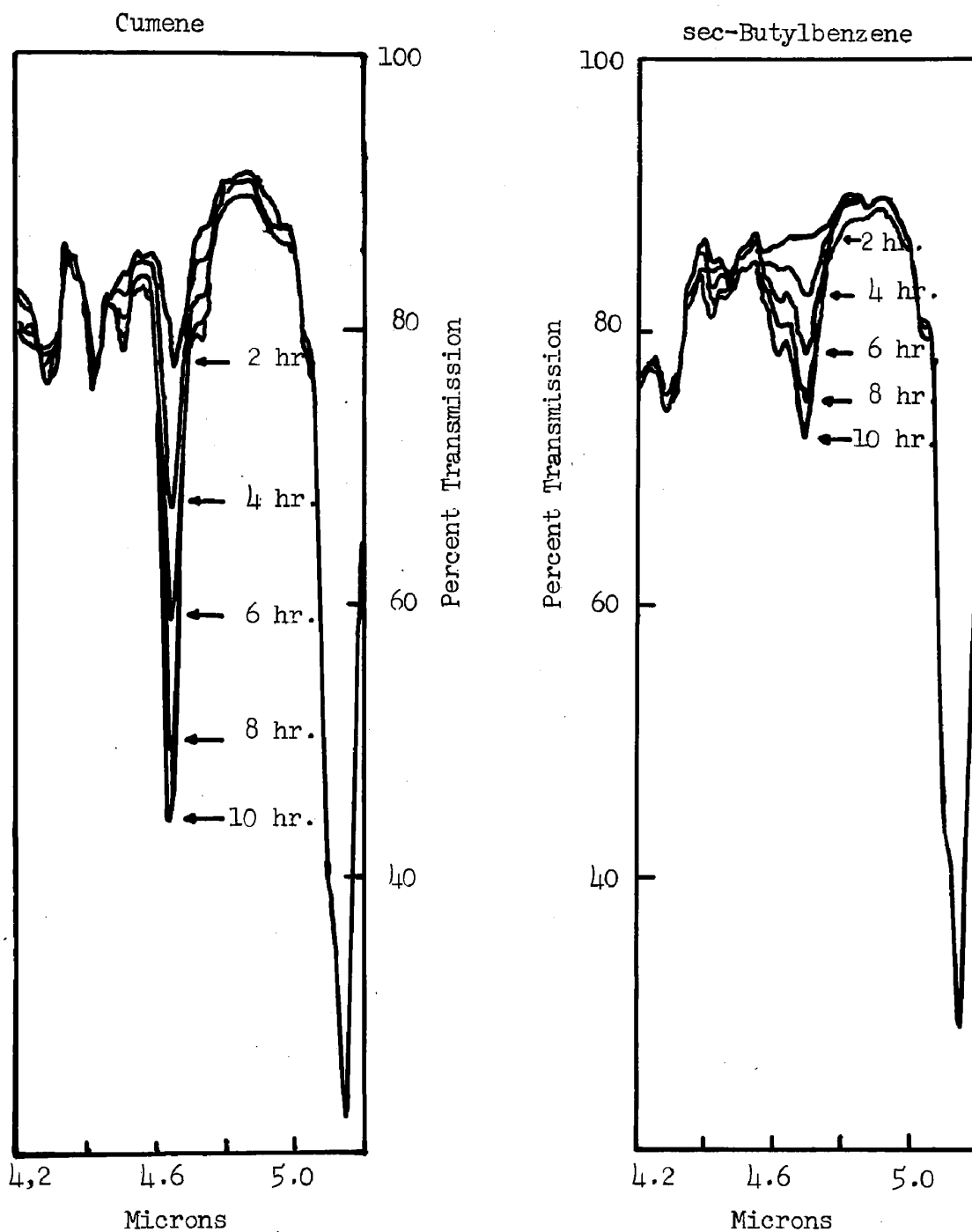
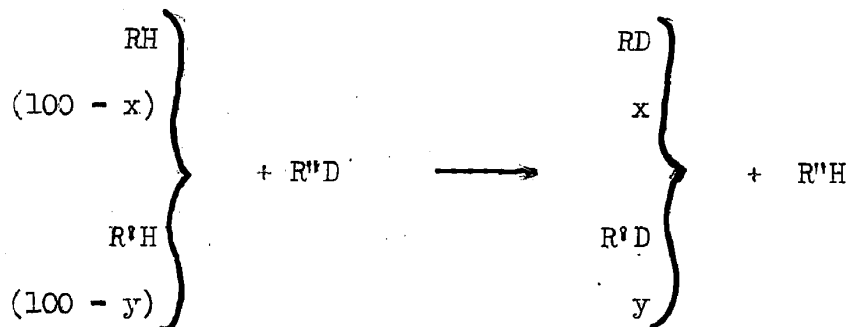


Figure 8. Aliphatic C-D stretching region showing progressive increase of deuterium content during a competition reaction between cumene and sec-butylbenzene using ethylbenzene- d_5 as deuterium source, potassium metal as catalyst and 150° as reaction temperature. (These data are tabulated in Table VII.)

Calculation of Rate Constants

The rate constants were calculated using the values for deuterium exchange found in Tables VII and XI-XV. The over-all equation for initial exchange of equimolar quantities of two hydrocarbons (RH and R'H) with a third containing deuterium (R"D) may be written:



where

x = percent of RD at time t

y = percent of R'D at time t

$100 - x$ = percent of RH at time t

$100 - y$ = percent of R'H at time t

The first order kinetic equation (44),

$$k = \frac{2.303}{t} \log \frac{100}{100 - \%D}$$

where %D is either x or y was used for the calculation of the reaction rate constant, k , for each exchange.

Tables VIII and IX list the values obtained from this equation, together with the value of each run as determined by the least squares slope (45) of $\log (100/100 - \%D)$ versus time for cumene and sec-butylbenzene. Corresponding tables for the other exchanges may be found

in the Appendix. Figure 9 shows a typical least squares plot.

In most cases, samples for duplicate points were run at the same time to be assured of equal exchange conditions. In one instance, however, two separate runs were made several weeks apart, each consisting of five samples (2, 4, 6, 8 and 10 hours). These data are in Tables VII, VIII and IX. The average rate constants for cumene were 5.27×10^{-6} and 5.39×10^{-6} and for sec-butylbenzene, 2.49×10^{-6} and 2.39×10^{-6} . It is apparent that the rate constants were fairly reproducible.

Table X lists the relative rates of exchange for all hydrocarbons studied, a value of 1.00 being assigned to the hydrocarbon with the slowest exchange rate (2,2-dimethyl-3-phenylbutane).

Mechanism

Any adequate interpretation of the data assembled in the present investigation would be supplemented by a knowledge of the reaction mechanism (46). Several different mechanisms of metalation have been advanced in recent years, the main difference being the relative importance of the role played by the alkali metal. From their physical properties it appears that alkyl- and aryl-potassium compounds are polar and behave as undissociated ion-pairs (1). Morton (47-51) has visualized side-chain metalation of alkylaromatics as an electrophilic process where the leading role was that of the alkali-metal cation, the anion aiding but relegated to a minor part. In this interpretation the residual polarity of the metal cation attracts the electrons of the carbon-hydrogen covalent bond in the side chain, thus loosening the

TABLE VIII

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO CUMENE
IN COMPETITION WITH *sec*-BUTYLBENZENE

(Deuterium source: ethylbenzene- d_5 ; catalyst: potassium
metal; temperature: 150°; reaction vessel: sealed tubes.

Data calculated from Table VII.)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	--	--
2	7200	2.5	0.01098	3.51
3*	7200	3.0	0.01322	4.23
4	14400	8.2	0.03715	5.94
5*	14400	7.0	0.03153	5.04
6	21600	11.2	0.05158	5.50
7*	21600	12.2	0.05652	6.10
8	28800	16.5	0.07831	6.26
9*	28800	15.4	0.07262	5.81
10	36000	16.8	0.07986	5.11
11*	36000	18.7	0.08991	5.75
Average				5.33 ± 0.68
Least Squares Slope				5.64

*These were run two weeks after the even-numbered samples.

TABLE IX

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO *sec*-BUTYLBENZENE
IN COMPETITION WITH CUMENE

(Deuterium source: ethylbenzene- d_5 ; catalyst: potassium metal;
temperature: 150°; reaction vessel: sealed tubes. Data calculated
from Table VII.)

Sample	Time (sec.)	Percent D	Lcg (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	--	--
2	7200	1.9	0.00834	2.67
3*	7200	1.6	0.00702	2.25
4	14400	3.9	0.01728	2.76
5*	14400	2.6	0.01144	1.83
6	21600	4.3	0.01907	2.03
7*	21600	5.8	0.02596	2.77
8	28800	7.2	0.03246	2.60
9*	28800	7.5	0.03387	2.71
10	36000	8.2	0.03715	2.38
11*	36000	8.3	0.03763	2.41
Average				2.44 \pm 0.26
Least Squares Slope				2.43

*These were run two weeks after the even-numbered samples.

Figure 9. Least squares slopes showing rates of deuterium exchange competition between cumene and sec-butylbenzene (see Tables VII, VIII and IX).

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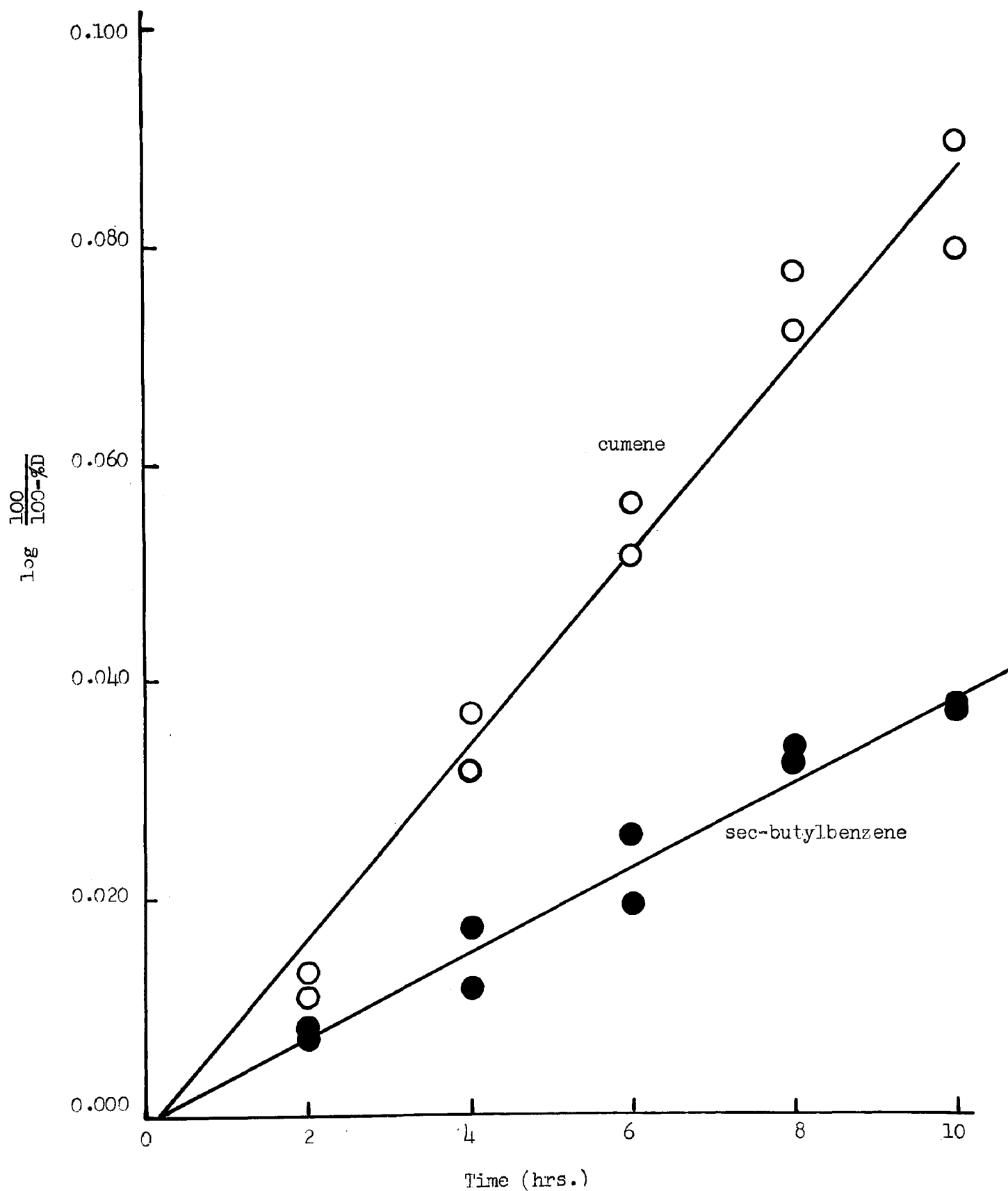
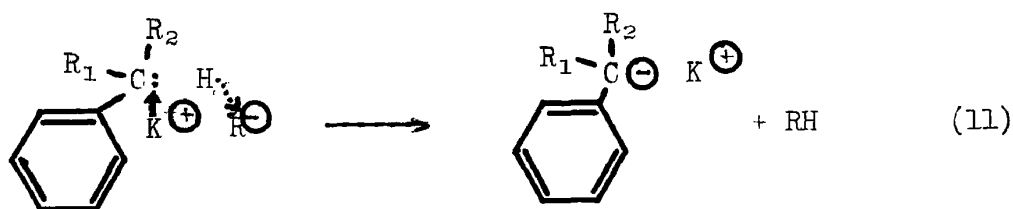


TABLE X
RELATIVE DEUTERIUM EXCHANGE RATES CALCULATED FROM
LEAST SQUARES SLOPES
(2,2-dimethyl-3-phenylbutane = 1.00)

Number	Hydrocarbon	Relative Exchange Rate
1	2,2-dimethyl-3-phenylbutane	1.00
2	2-methyl-3-phenylbutane	1.90
3	3-phenylpentane	1.96
4	2-phenylpentane	6.91
5	sec-butylbenzene	8.13
6	cumene	18.9

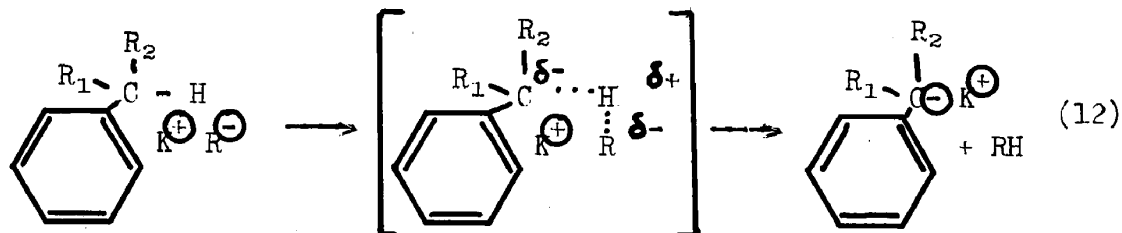
proton which is then received by the anion in a "push-pull" type of reaction. This is illustrated below using Morton's notation of a heavy arrow indicating a major force (R , R_1 and R_2 are alkyl groups):



Electrophilic attack by organoalkali reagents was explained by Morton with this mechanism.

Bryce-Smith (5), on the other hand, has suggested that the anion is the more important species and visualizes a tetrapolar transition state where the function of the metal cation is purely electrostatic,

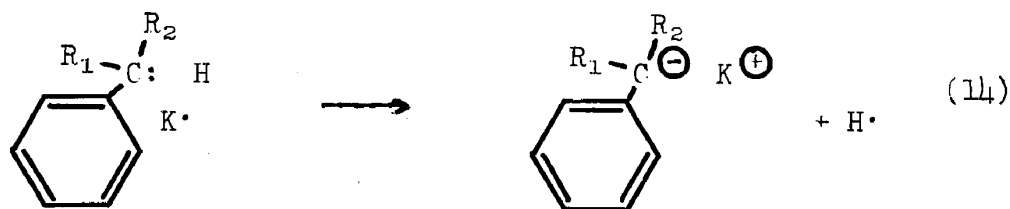
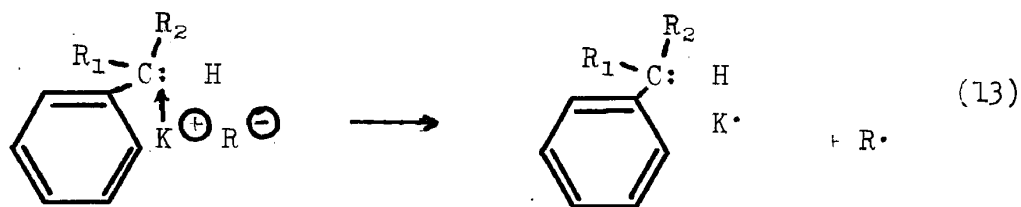
the driving force for the reaction being the energy difference between carbanions. This concept is illustrated below:



Bryce-Smith has termed this type of substitution "protophilic," involving the removal of a proton in the rate-determining step. This is to be distinguished from a nucleophilic substitution involving RK which would involve attack on carbon by R^- with subsequent removal of a hydride ion. As a test of this mechanism, Bryce-Smith (52) studied the metalation of deuterobenzene and toluene- d_9 by ethylpotassium. He found that protium was replaced by potassium more rapidly than deuterium, indicating that, indeed, the breaking of the carbon-hydrogen bond is important in the rate-determining step. He further points out that the rate of metalation at a given position is related to the acidity of the hydrogen which is replaced. Objections raised by Bryce-Smith to Morton's proposed scheme include the fact that the metal cation retains the same electronic configuration after reaction as before and that an electrophilic attack by the metal cation is not in agreement with the extensive meta-substitution obtained in the metalation of cumene by ethylpotassium nor with the fact that alkyl groups appear to deactivate the ring to substitution.

In an attempt to do away with the objections of Bryce-Smith, Morton (47,53) supplemented his previous mechanism with an alternative route, the reaction conditions determining which process would

predominate. This additional path involves the concept of a radical-pair as opposed to an ion-pair. Here, the first step is assumed to be the dissociation of the organoalkali salt (with the hydrocarbon coordinated on the cation) into two radicals, followed by the removal of the most acidic hydrogen in the hydrocarbon by atomic alkali metal. The process is terminated by acceptance of this hydrogen atom by the alkyl radical. This sequence is shown in the following equations:



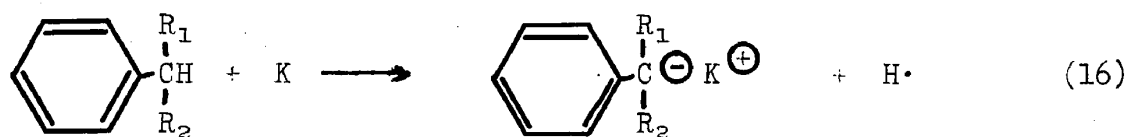
Morton pointed out that this alternative process is in agreement with the removal of a proton in the rate-determining step. This mechanism is regarded by Bryce-Smith (54) as untenable since Morton did not supply direct experimental evidence for free radicals and because of other conflicting evidence.

Regardless of which mechanism is correct, both investigators agree that the relative ease of metalation at any given position is a function of the acidity of the hydrogen being displaced, or, stated another way, the salt of the strongest acid should be formed. With this fact in mind, the present investigation was undertaken in an attempt to

correlate the relative acidity of certain hydrocarbon acids with their structure.

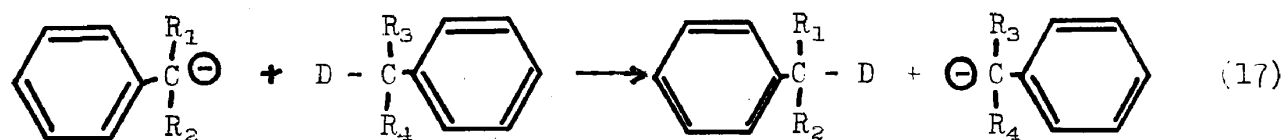
Several processes are evident in the exchange reactions studied (17): (1) the initial attack of the catalyst on an alpha hydrogen to form the organoalkali compound, (2) the exchange reaction between a hydrocarbon and a carbanion and/or (3) exchange between inorganic hydride and an alkylaromatic. Only by these paths can the observed products be rationalized.

The first step, attack by catalyst, may be visualized as follows:



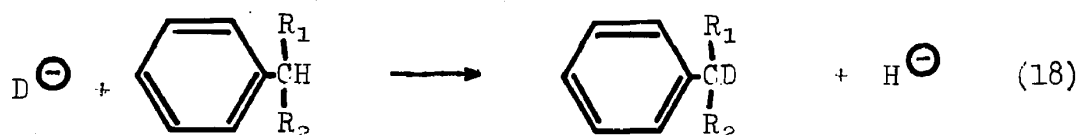
The hydrogen (or deuterium) atom formed can either unite with a second hydrogen (or deuterium) atom to form hydrogen gas, or with an atom of potassium to form potassium hydride (or deuteride). As has been previously mentioned, attack occurs on the alpha carbon due to resonance stabilization of the resulting benzyl carbanion.

The next likely process is the transfer of an alpha proton (or deuteron) from a hydrocarbon to a carbanion resulting in a new, less basic carbanion and less acidic hydrocarbon. This is illustrated below:



A consequence of path (17) is that if equal concentrations of carbanions of different basicities (i.e. α,α -dimethylbenzyl and α -ethyl- α -methylbenzyl) were to compete for a source of deuterium (i.e. ethylbenzene- d_α), the less acidic hydrocarbon formed (presumably, sec-butylbenzene) should acquire deuterium more rapidly, other factors being equal.

Another possible path for exchange is the direct attack of a deuteride ion on the alpha hydrogen of a hydrocarbon, as indicated:



Unfortunately at the present time, reaction (18) cannot be definitely ruled out as a possible process (although there is little precedence for this type of reaction). It seems probable that this path would likewise be a measure of the hydrocarbon acidity, leading to the same results as step (17) (the less acidic hydrocarbon exchanging with deuterium at a faster rate). It will be assumed in further discussion that exchange occurs predominantly according to (17). All three paths are consistent with first-order kinetics.

From a consideration of the electrical effects of the various α,α -dialkyl groups on the hydrocarbons studied, qualitative predictions as to the order of relative acidity can be made. The order of decreasing electron repulsion (inductive effect) is $-\text{C}(\text{CH}_3)_3 > -\text{CH}(\text{CH}_3)_2 > -\text{CH}_2\text{CH}_3 > -\text{CH}_3$ (55). This leads to an order of decreasing relative acidity as follows: cumene $>$ sec-butylbenzene \approx 2-phenylpentane $>$ 3-phenylpentane and 2-methyl-3-phenylbutane $>$ 2,2-dimethyl-3-phenylbutane.

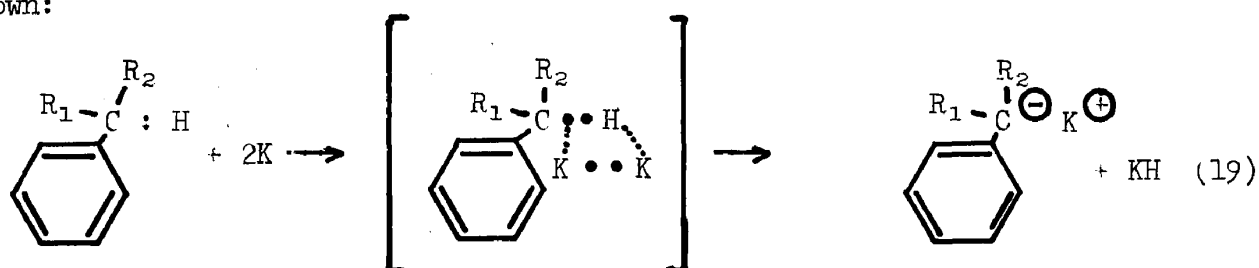
If step (17) is the rate-determining one, the deuterium exchange rates should increase in the order of decreasing acidity. The results obtained are completely reversed from this observation, the order of decreasing rates paralleling that of predicted decreasing acidity.

The observed results can, however, be rationalized by assuming that step (16), initiation of the exchange by catalyst, is rate-determining. This seems entirely reasonable from the fact decreasing the amount of catalyst decreased the rate of exchange. Further, it is felt that this step is directly related to the acidity of the hydrogen displaced, the more acidic hydrogen being more easily removed (resulting in a higher concentration of the less basic carbanion). This belief is similar to Robert's (8) assumption that the rate constants for removal of particular hydrogens in acids of similar structure are related to their equilibrium ionization constants, K_a .

It will be noted that the steric requirements of the hydrocarbons studied increase with decreasing acidity. Because of this, it might be argued that the decrease in rate of deuterium exchange is due solely to a steric factor. If step (16) (attack by a potassium atom) is the rate-determining step as postulated, steric considerations would be expected to play a less dominant role than if path (17) (attack by a carbanion) were the controlling step. It is, however, difficult to divorce the steric factors from any of the processes which may be taking place. Bryce-Smith (5) studied the competitive metalation reaction of cumene and ethylpotassium and assigned the order of decreasing relative acidity to the hydrogens on cumene para > meta > alpha > ortho > > beta.

These results are not compatible with those obtained by deuterium exchange where substitution occurred almost exclusively in the alpha position. Bryce-Smith's results may be due to several factors, some of which are not directly related to the acidity. One is that the ethyl carbanion, being very basic, is not as discriminating as a potassium atom when displacing a hydrogen. Therefore, the likelihood of proton removal from the ring is greater. Secondly, the steric requirement of the ethyl carbanion (probably functioning as an ion-pair with the potassium cation) is considerably greater than a potassium atom. This would tend to reduce the probability of attack in the alpha position and yet have little effect on the meta and para positions.

The initial attack, equation (16), need not involve free radicals, the process very likely being concerted where the hydrogen atom being expelled is aided by a second potassium atom. This may be pictured as shown:



The reaction most probably occurs on the surface of the liquid potassium metal.

Further study on this problem might help to elucidate the mechanism. A more extensive investigation into the effect varying amounts of catalyst produce on the rate of exchange would be of value in the

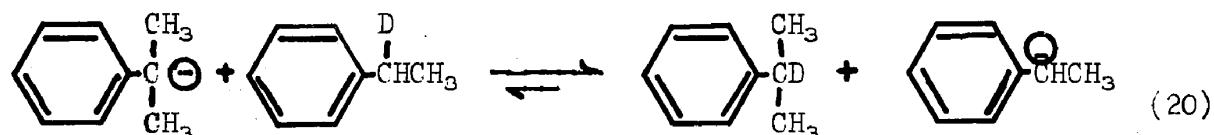
establishment of step (16) as rate-determining. The question of whether the hydrogen atom displaced in the initial attack forms hydrogen gas or potassium hydride could be resolved by analysis for hydrogen gas. Another test for the postulated mechanism would be the addition of deuteride ion to the reaction mixture. The rate should not change (provided the total source of deuterium was constant) if path (16) is rate-determining, whereas if (18) were involved, a rate increase would be observed.

In conclusion, it is felt that the relative rates tabulated in Table X represent the relative acidities of these hydrocarbons as measured by deuterium exchange over potassium metal.

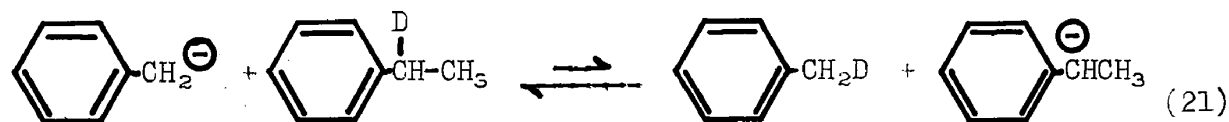
Deuterium exchange as a method for measuring acidity can be extended to include a wide variety of compounds. Those particularly suited are hydrocarbons containing benzylic hydrogens. An interesting series of compounds to study might be alkylaromatics, such as cumene, mono- or di-substituted in the various ring positions by groups which would not react with potassium, but would be expected to influence the acidity. The tert-butyl and phenyl groups are two such substituents. The special advantage such a system offers, at least when the ortho positions are unsubstituted, is that the steric requirements of all compounds in this series (i.e. ring substituted cumenes) would be the same.

Another interesting competitive exchange reaction would be that of toluene and cumene using ethylbenzene- d_4 as the deuterium source. Toluene is the most acidic and cumene the least acidic of the three

hydrocarbons. Because of this, the concentration of benzyl carbanions present in the reaction mixture should exceed those of α -phenylisopropyl carbanions, implying that toluene would exchange faster. The deuterium exchange between ethylbenzene- d_α and the anion from cumene would be expected to proceed normally, the driving force being the formation of the less basic carbanion (α -phenylethyl) and the less acidic hydrocarbon (cumene). Equilibrium should be on the right side of the equation below:



However, in order for exchange to occur between ethylbenzene- d_α and the anion from toluene the exchange involves the production of the more basic anion (α -phenylethyl) and the more acidic hydrocarbon (toluene). Equilibrium here should lie on the left of the following equation:



A study of these rates might show that in this reaction, path (17) (deuterium exchange) becomes rate-determining for toluene while cumene is still dependent upon step (16) (attack by potassium). The net result may be that cumene would have the greater over-all exchange rate in spite of the fact that it is less acidic. This would provide an interesting test of the proposed mechanism.

SUMMARY

SUMMARY

1. A general synthetic route to alpha-deuterated alkylaromatic hydrocarbons was developed. This involved cleavage of the appropriate arylalkyl methyl ether with potassium metal and hydrolysis of the resulting organometallic with deuterium oxide. Compounds prepared by this method contained little or no deuterium on the aromatic ring. The following hydrocarbons were synthesized using this procedure: cumene-d_α, sec-butylbenzene-d_α, 2-phenylpentane-d_α, 3-phenylpentane-d_α, 2-methyl-3-phenylbutane-d_α and 2,2-dimethyl-3-phenylbutane-d_α. These standards were analyzed mass spectrometrically and then used for preparing calibration curves from which unknown amounts of deuterium could be determined.

2. A gas chromatography apparatus was adapted so that small volumes of hydrocarbon mixtures could be separated with near-quantitative recovery of the individual components.

3. Alkylaromatics, when heated in the presence of a suitable catalyst such as potassium metal, may exchange hydrogens on the carbon alpha to the aromatic ring. This reaction was investigated as a possible method for determining the relative acidity of hydrocarbons. The technique involved measuring the relative rates at which two hydrocarbons compete for the deuterium in a third.

4. In preliminary experiments, the effects of several catalysts, temperature ranges, reaction vessels and compound types were studied. The exchange rates varied directly with the amount of catalyst and also

depended upon the molar ratio of the hydrocarbon reactants. Conditions most suitable for kinetic experiments involved heating two hydrocarbons with ethylbenzene- d_6 for varying times at 150° in sealed tubes using potassium metal as the catalyst.

5. First order rate constants were obtained from plots of $\log (100/100-\%D)$ vs. t , when $\%D$ was the mole percent of deuterium in the hydrocarbon at time t . The order of decreasing relative exchange rates was found to be: cumene, 18.9; sec-butylbenzene, 8.13; 2-phenylpentane, 6.91; 3-phenylpentane, 1.96; 2-methyl-3-phenylbutane, 1.90; 2,2-dimethyl-3-phenylbutane, 1.00. This order parallels that of predicted acidity of these compounds.

6. A mechanism is proposed which accommodates the results obtained. This involves a rate-determining attack by potassium on the most acidic hydrogen of each compound to form the organopotassium salt followed by deuterium transfer between the carbanion of an organometallic and a deuterated hydrocarbon molecule. Both steps are believed to depend on the acidity of the hydrocarbons.

7. In miscellaneous experiments, diphenylmethane did not exchange protium for deuterium with ethylbenzene- d_6 under a variety of conditions. An explanation for this is offered. An attempted competition reaction between cumene and phenylcyclopropane under the exchange conditions resulted in deuterium transfer to cumene but polymerization of phenylcyclopropane.

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LITERATURE CITED

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APPENDIX

Figure 10. Percent deuterium content of mixtures of cumene and cumene- d_9 in carbon tetrachloride vs. optical density at 4.65 microns. (Concentration of hydrocarbon = 2.97 M.)

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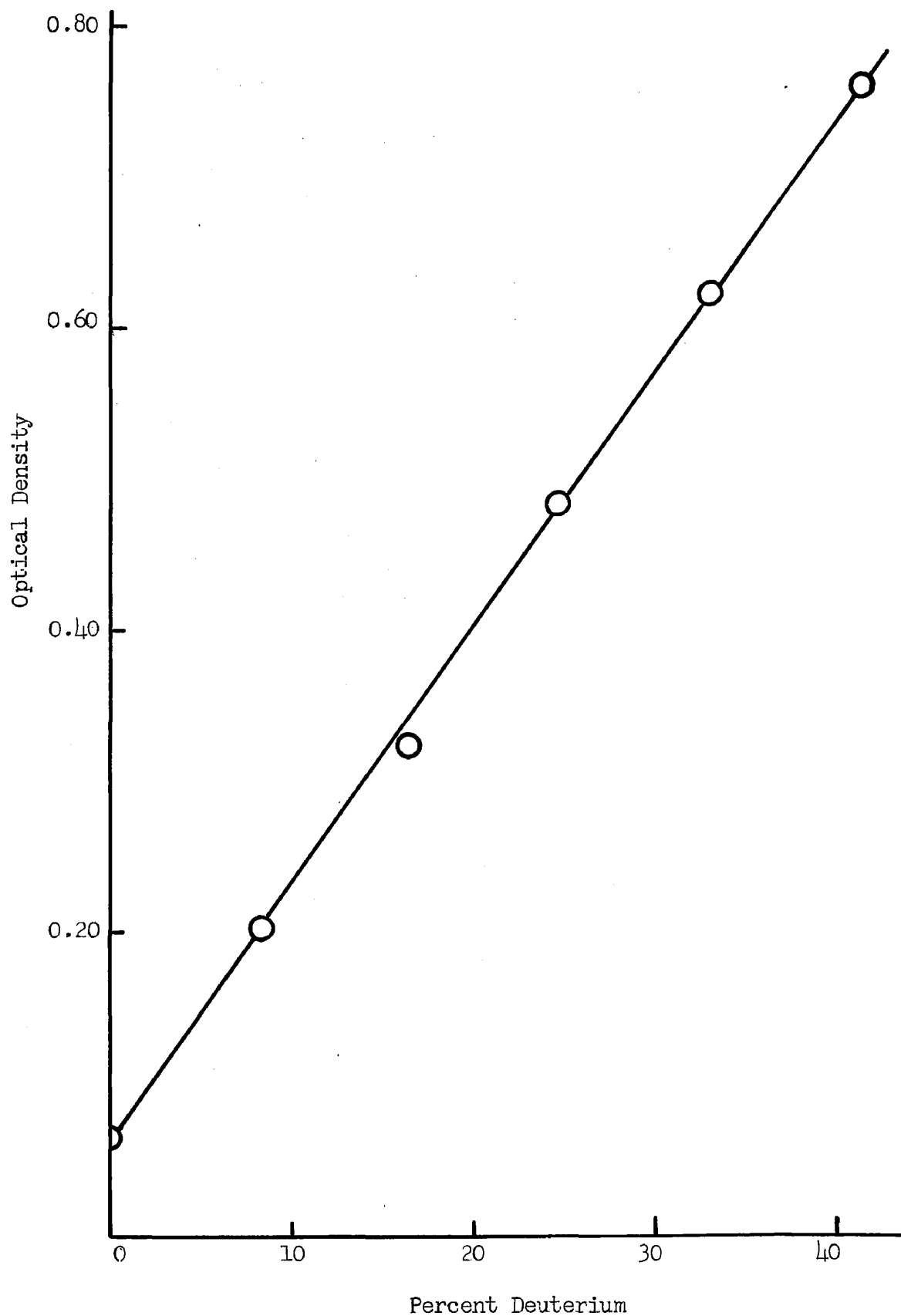


Figure 11. Percent deuterium content of mixture of 3-phenylpentane, and 3-phenylpentane- d_4 in carbon tetrachloride vs. optical density at 4.68 microns. (Concentration of hydrocarbon = 2.40 M.)

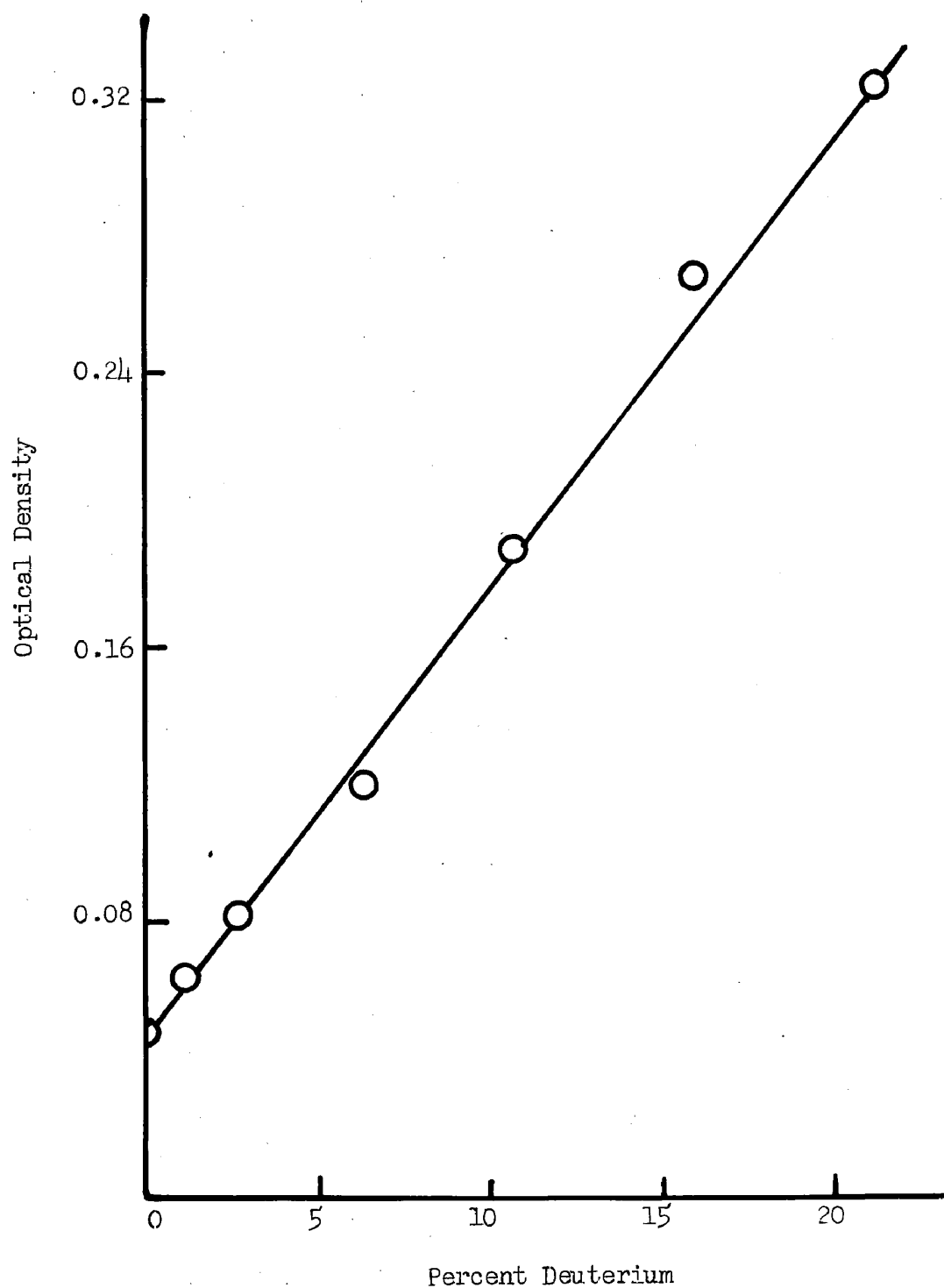


Figure 12. Percent deuterium content of mixtures of 2-phenylpentane and 2-phenylpentane- d_4 in carbon tetrachloride vs. optical density at 4.67 microns. (Concentration of hydrocarbon = 2.39 M.)

85

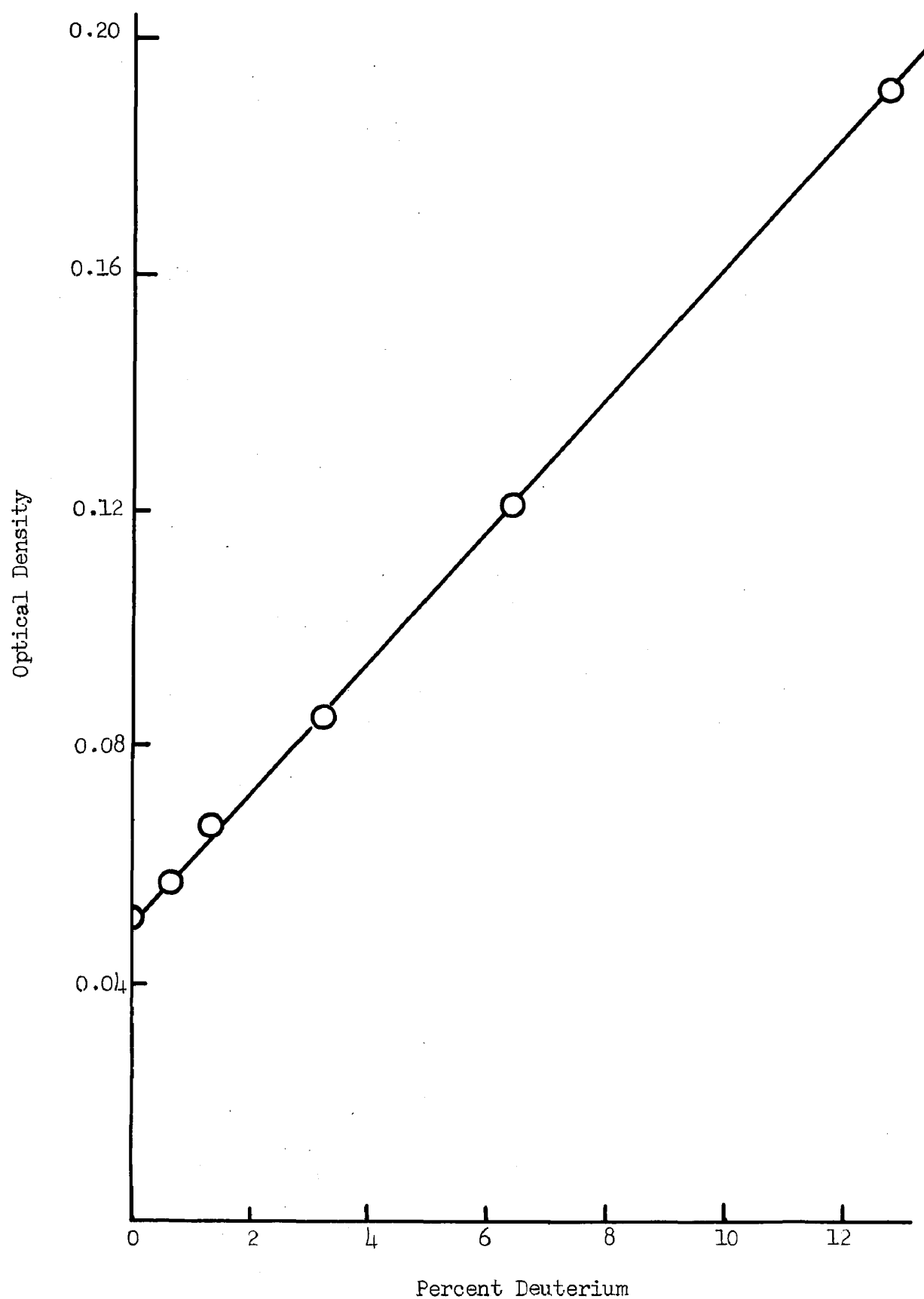


Figure 13. Percent deuterium content of mixtures of 2-methyl-3-phenylbutane and 2-methyl-3-phenylbutane- d_4 in carbon tetrachloride vs. optical density at 4.70 microns. (Concentration of hydrocarbon = 2.42 M.)

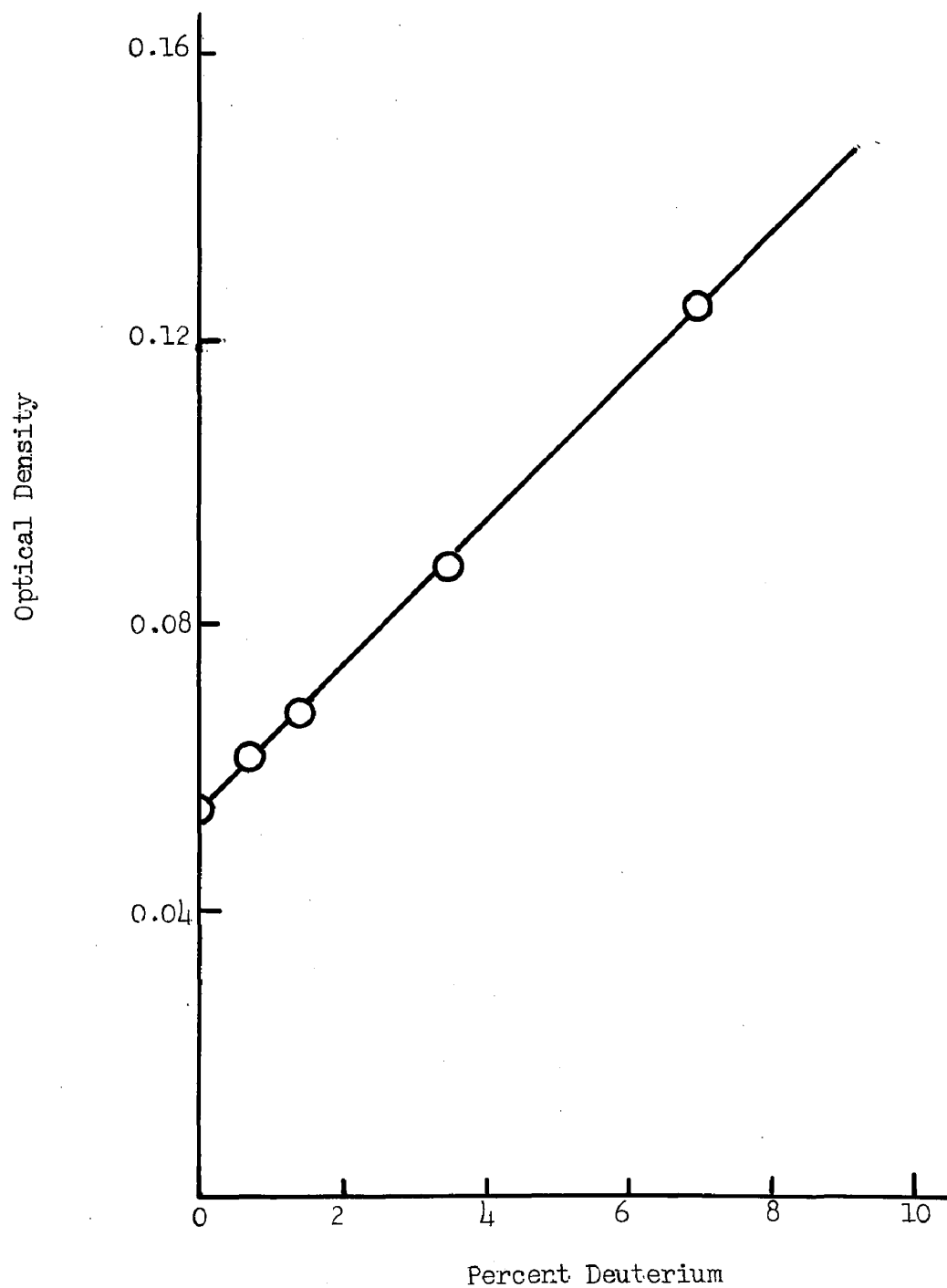


Figure 14. Percent deuterium content of mixtures of 2,2-dimethyl-3-phenylbutane and 2,2-dimethyl-3-phenylbutane- d_4 in carbon tetrachloride vs. optical density at 4.69 microns. (Concentration of hydrocarbon = 4.16 M.)

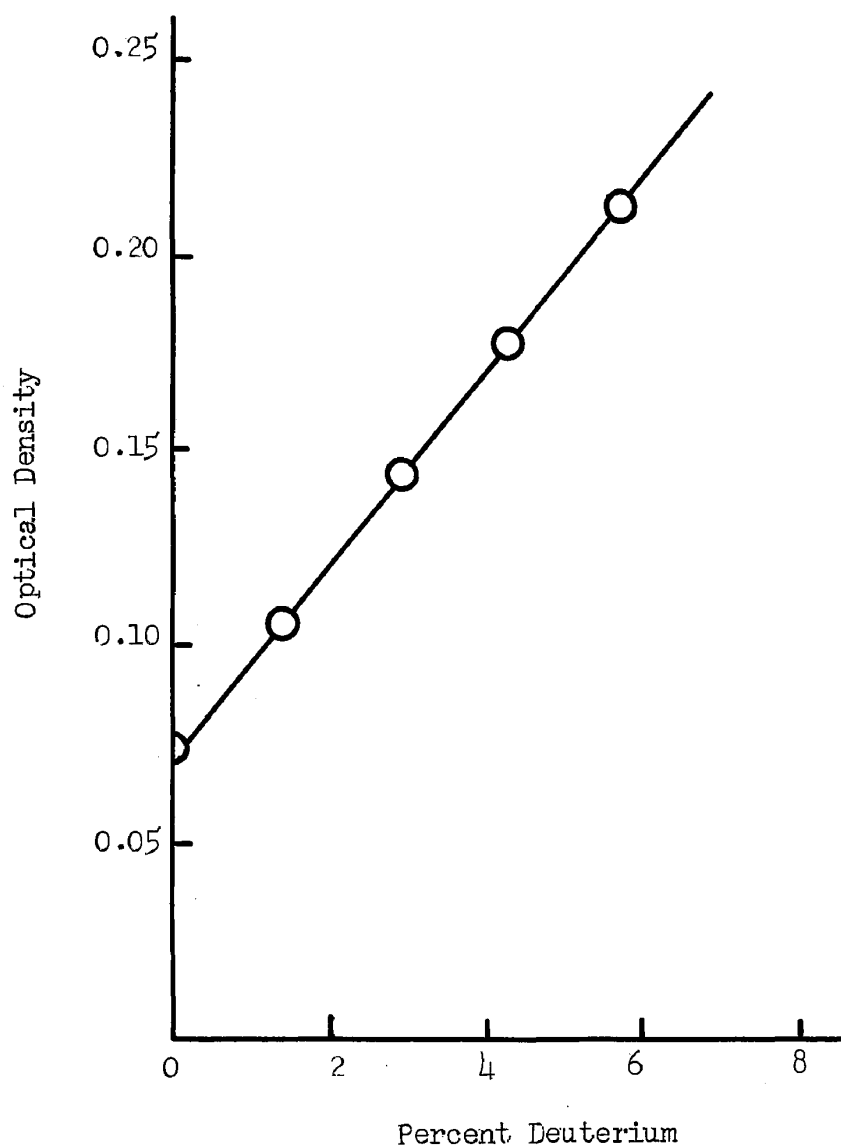


TABLE XI

COMPETITION BETWEEN CUMENE AND sec-BUTYLBENZENE
 (0.10 g. potassium metal, 150°, 1.200 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Weight (g.)	Percent Deuterium Exchanged	
			Cumene	sec-Butylbenzene
1	2	0.104	0.7	1.1
2	4	0.103	5.3	2.2
3	6	0.096	10.1	4.9
4	8	0.102	11.0	4.6
5	10	0.104	14.2	6.3

*Stock solution: 1.840 ml. ethylbenzene-d₆, 2.100 ml. cumene
 2.340 ml. sec-butylbenzene.

TABLE XII

COMPETITION BETWEEN *sec*-BUTYLBENZENE AND 3-PHENYLPENTANE
(0.20 g. potassium metal, 150°, 1.400 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Weight (g.)	Percent Deuterium Exchanged	
			<i>sec</i> -Butylbenzene	3-Phenylpentane
1	2	0.209	2.1	0.7
2	4	0.199	3.7	0.9
3	4	0.205	4.1	0.9
4	6	0.204	6.0	1.5
5	6	0.204	5.6	1.4
6	8	0.205	6.6	1.7
7	8	0.207	6.7	1.7
8	10	0.199	8.6	2.0
9	10	0.207	8.3	2.1

*Stock solution: 5.00 ml. ethylbenzene- d_6 , 4.470 ml. *sec*-butylbenzene, 4.950 ml. 3-phenylpentane.

TABLE XIII

COMPETITION BETWEEN *sec*-BUTYLBENZENE AND 2-PHENYLPENTANE
(0.20 g. potassium metal, 150°, 1.400 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Weight (g.)	Percent Deuterium Exchanged	
			<i>sec</i> -Butylbenzene	2-Phenylpentane
1	2	0.206	3.0	2.6
2	2	0.208	1.9	1.8
3	4	0.203	4.0	3.4
4	4	0.201	4.3	3.7
5	6	0.201	6.5	6.1
6	6	0.200	6.2	5.6
7	8	0.206	8.0	6.8
8	8	0.202	8.3	7.0
9	10	0.203	8.7	7.1
10	10	0.206	7.8	6.7

*Stock solution: 5.000 ml. ethylbenzene- d_5 , 4.470 ml. *sec*-butylbenzene, 4.960 ml. 2-phenylpentane.

TABLE XIV

COMPETITION BETWEEN sec-BUTYL BENZENE AND 2-METHYL-3-PHENYLBUTANE
(0.20 g. potassium metal, 150°, 1.440 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Weight (g.)	Percent Deuterium Exchanged	
			sec-Butylbenzene	2-Methyl-3-phenylbutane
1	2	0.204	2.2	0.8
2	3	0.203	3.5	0.6
3	4	0.203	3.9	0.9
4	6	0.201	6.2	1.5
5	6	0.205	6.0	1.7
6	8	0.204	7.2	1.9
7	10	0.205	9.7	2.4
8	10	0.207	8.5	1.9
9	15	0.200	12.1	3.0
10	20	0.205	15.2	3.7

*Stock solution: 5.500 ml. ethylbenzene-d₆; 4.917 ml. sec-butylbenzene; 5.390 ml. 2-methyl-3-phenylbutane.

TABLE XV

COMPETITION BETWEEN sec-BUTYLBENZENE AND 2,2-DIMETHYL-3-PHENYLBUTANE
(0.20 g. potassium metal, 150°, 1.500 ml. stock solution* per ampoule)

Sample	Time (hrs.)	Potassium Weight (g.)	Percent Deuterium Exchanged	
			sec-Butylbenzene	2,2-Dimethyl-3-phenyl- butane
1	2	0.299	3.0	0.4
2	2	0.300	2.6	0.3
3	4	0.298	4.7	0.6
4	4	0.302	4.8	0.7
5	6	0.303	6.6	0.8
6	6	0.301	6.6	0.8
7	8	0.306	7.8	0.9
8	8	0.301	7.8	0.9
9	10	0.303	9.1	1.0
10	10	0.302	7.8	1.3

*Stock solution: 6.000 ml. ethylbenzene-d₅; 4.470 ml. sec-butylbenzene; 5.180 ml. 2,2-dimethyl-3-phenylbutane.

TABLE XVI

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO CUMENE
IN COMPETITION WITH sec-BUTYLBENZENE
(Data calculated from Table XI.)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	$(\times 10^{-6}) k_1$ (sec. ⁻¹)
1	0	0	---	---
2	7200	0.7	0.00303	0.97
3	14400	5.3	0.02366	3.78
4	21600	10.1	0.04622	4.93
5	28800	11.0	0.05061	4.05
6	36000	14.2	0.06651	4.26
Average				3.60 ± 1.05
Least Squares Slope				4.21

TABLE XVII

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 sec-BUTYLBENZENE IN COMPETITION WITH CUMENE
 (Data calculated from Table XI)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	1.1	0.00479	1.53
3	14400	2.2	0.00966	1.55
4	21600	4.9	0.02181	2.33
5	28800	4.6	0.02044	1.63
6	36000	6.3	0.02825	1.81
Average				1.77 ± 0.24
Least Squares Slope				1.82

TABLE XVIII

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 sec-BUTYLBENZENE IN COMPETITION WITH 3-PHENYLPENTANE
 (Data calculated from Table XII)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	2.1	0.00924	2.96
3	14400	3.7	0.01636	2.62
4	14400	4.1	0.01820	2.91
5	21600	6.0	0.02686	2.86
6	21600	5.6	0.02502	2.67
7	28800	6.6	0.02967	2.37
8	28800	6.7	0.03011	2.41
9	36000	8.6	0.03906	2.50
10	36000	8.3	0.03763	2.41
Average				2.54 ± 0.20
Least Squares Slope				2.51

TABLE XIX

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
3-PHENYLPENTANE IN COMPETITION WITH sec-BUTYLBENZENE
(Data calculated from TABLE XII)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	$(\times 10^{-6}) k_1$ (sec. ⁻¹)
1	0	0	---	---
2	7200	0.7	0.00303	0.969
3	14400	0.9	0.00393	0.629
4	14400	0.9	0.00393	0.629
5	21600	1.5	0.00655	0.698
6	21600	1.4	0.00612	0.653
7	28800	1.7	0.00745	0.596
8	28800	1.7	0.00745	0.596
9	36000	2.0	0.00877	0.561
10	36000	2.1	0.00924	0.591
Average				0.658 ± 0.078
Least Squares Slope				0.607

TABLE XX

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 sec-BUTYLBENZENE IN COMPETITION WITH 2-PHENYLPENTANE
 (Data calculated from Table XIII)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	3.0	0.01322	4.23
3	7200	1.9	0.00877	2.81
4	14400	4.0	0.01774	2.84
5	14400	4.3	0.01907	3.05
6	21600	6.5	0.02818	3.01
7	21600	6.2	0.02780	2.96
8	28800	8.0	0.03623	2.90
9	28800	8.3	0.03763	3.01
10	36000	8.7	0.03953	2.53
11	36000	7.8	0.03527	2.26
Average				2.96 ± 0.29
Least Squares Slope				2.71

TABLE XXI

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
2-PHENYLPENTANE IN COMPETITION WITH *sec*-BUTYLBENZENE
(Data calculated from Table XIII)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	2.6	0.011144	3.66
3	7200	1.8	0.00788	2.52
4	14400	3.4	0.01502	2.40
5	14400	3.7	0.01636	2.61
6	21600	5.6	0.02502	2.67
7	21600	6.1	0.02735	2.92
8	28800	6.8	0.03060	2.45
9	28800	7.0	0.03153	2.52
10	36000	6.7	0.02911	1.86
11	36000	7.1	0.03197	2.05
Average				2.57 ± 0.32
Least Squares Slope				2.31

TABLE XXII

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 sec-BUTYLBENZENE IN COMPETITION WITH 2-METHYL-3-PHENYLBUTANE
 (Data calculated from Table XIV)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	2.2	0.00966	3.09
3	10800	3.5	0.01549	3.30
4	14400	3.9	0.01728	2.76
5	21600	6.2	0.02780	2.96
6	21600	6.0	0.02686	2.86
7	28800	7.2	0.03246	2.60
8	36000	9.7	0.04430	2.83
9	36000	8.5	0.03858	2.47
10	54000	12.1	0.05603	2.39
11	72000	15.2	0.07159	2.29
Average				2.76 ± 0.25
Least Squares Slope				2.47

TABLE XXIII

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
2-METHYL-3-PHENYLBUTANE IN COMPETITION WITH sec-BUTYLBENZENE
(Data Calculated from Table XIV)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	0.8	0.00350	1.120
3	10800	0.6	0.00260	0.554
4	14400	0.9	0.00393	0.629
5	21600	1.5	0.00655	0.698
6	21600	1.7	0.00745	0.794
7	28800	1.9	0.00834	0.667
8	36000	2.4	0.01055	0.675
9	36000	1.9	0.00834	0.534
10	54000	3.0	0.01322	0.564
11	72000	3.7	0.01636	0.523
Average				0.676 ± 0.118
Least Squares Slope				0.579

TABLE XXIV

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 sec-BUTYLBENZENE IN COMPETITION WITH 2,2-DIMETHYL-3-PHENYLBUTANE
 (Data calculated from Table XV)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	2.6	0.01144	3.66
3	7200	3.0	0.01322	4.23
4	14400	4.7	0.02090	3.34
5	14400	4.8	0.02135	3.42
6	21600	6.6	0.02967	3.16
7	21600	6.6	0.02967	3.16
8	28800	7.8	0.03527	2.82
9	28800	7.8	0.03527	2.82
10	36000	9.1	0.04113	2.65
11	36000	7.8	0.03527	2.26
Average				3.15 ± 0.43
Least Squares Slope				2.77

TABLE XXV

FIRST ORDER RATE CONSTANTS FOR DEUTERIUM TRANSFER TO
 2,2-DIMETHYL-3-PHENYLBUTANE IN COMPETITION WITH *sec*-BUTYLBENZENE
 (Data calculated from Table XV)

Sample	Time (sec.)	Percent D	Log (100/100-%D)	k_1 ($\times 10^6$) (sec. ⁻¹)
1	0	0	---	---
2	7200	0.4	0.00174	0.557
3	7200	0.3	0.00131	0.417
4	14400	0.6	0.00262	0.418
5	14400	0.7	0.00305	0.488
6	21600	0.8	0.00349	0.372
7	21600	0.8	0.00349	0.372
8	28800	0.9	0.00393	0.314
9	28800	0.9	0.00393	0.314
10	36000	1.0	0.00436	0.279
11	36000	1.3	0.00568	0.364
Average				0.390 ± 0.065
Least Squares Slope				0.340

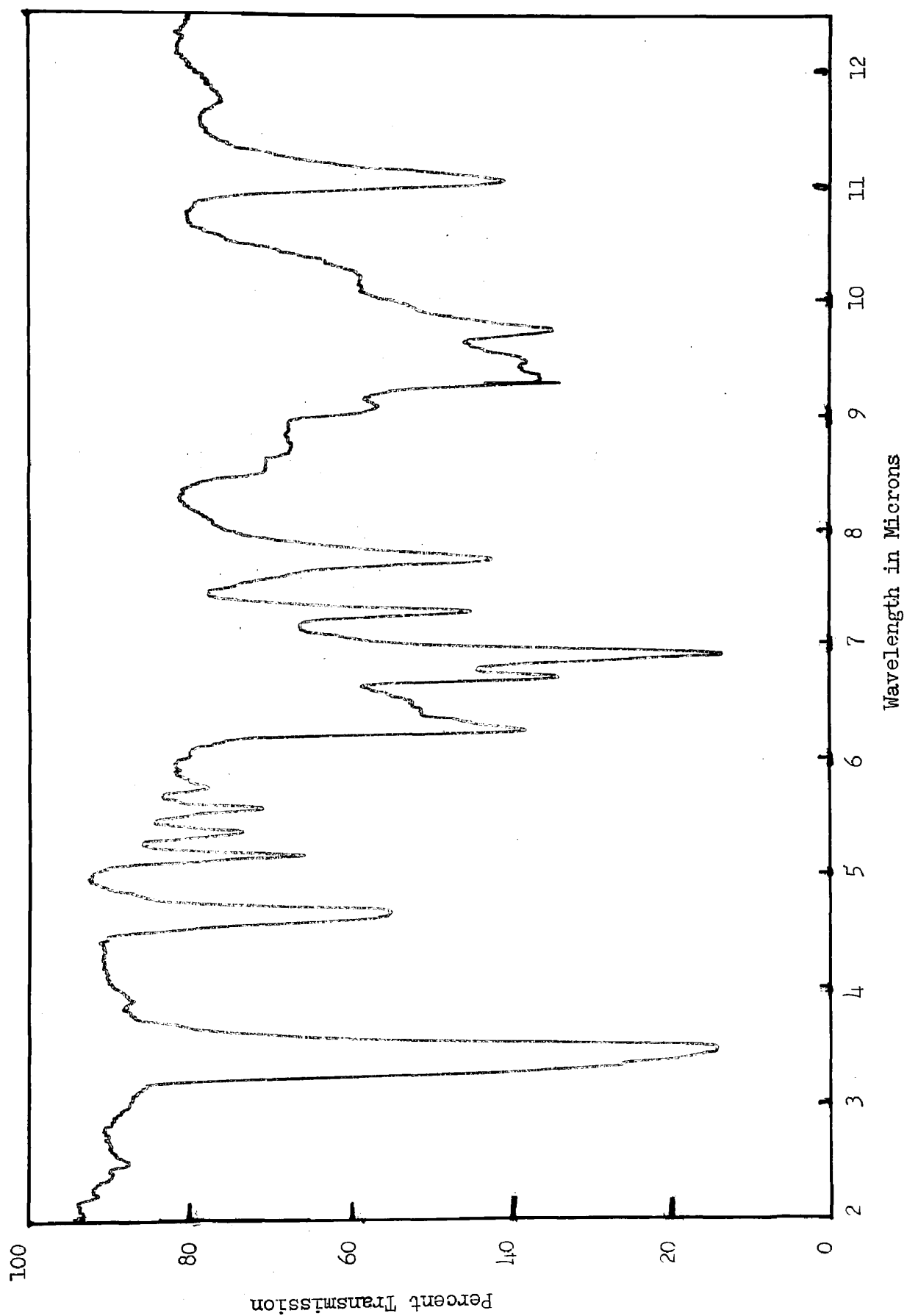


Figure 15. Infrared Spectrum of Ethylbenzene- d_9 (in Carbon Tetrachloride).

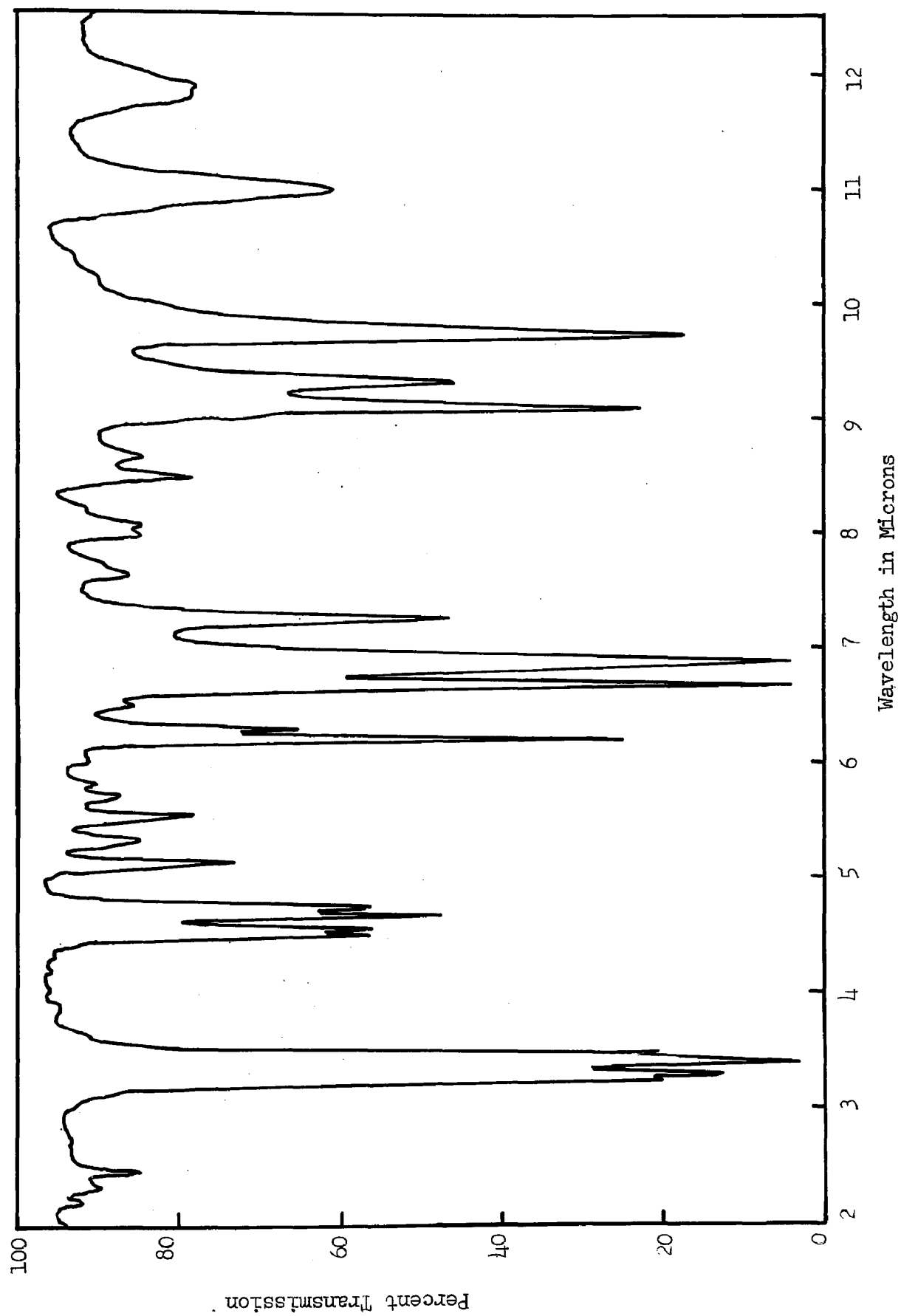


Figure 16. Infrared Spectrum of Ethylbenzene- d_5 , α (pure liquid).

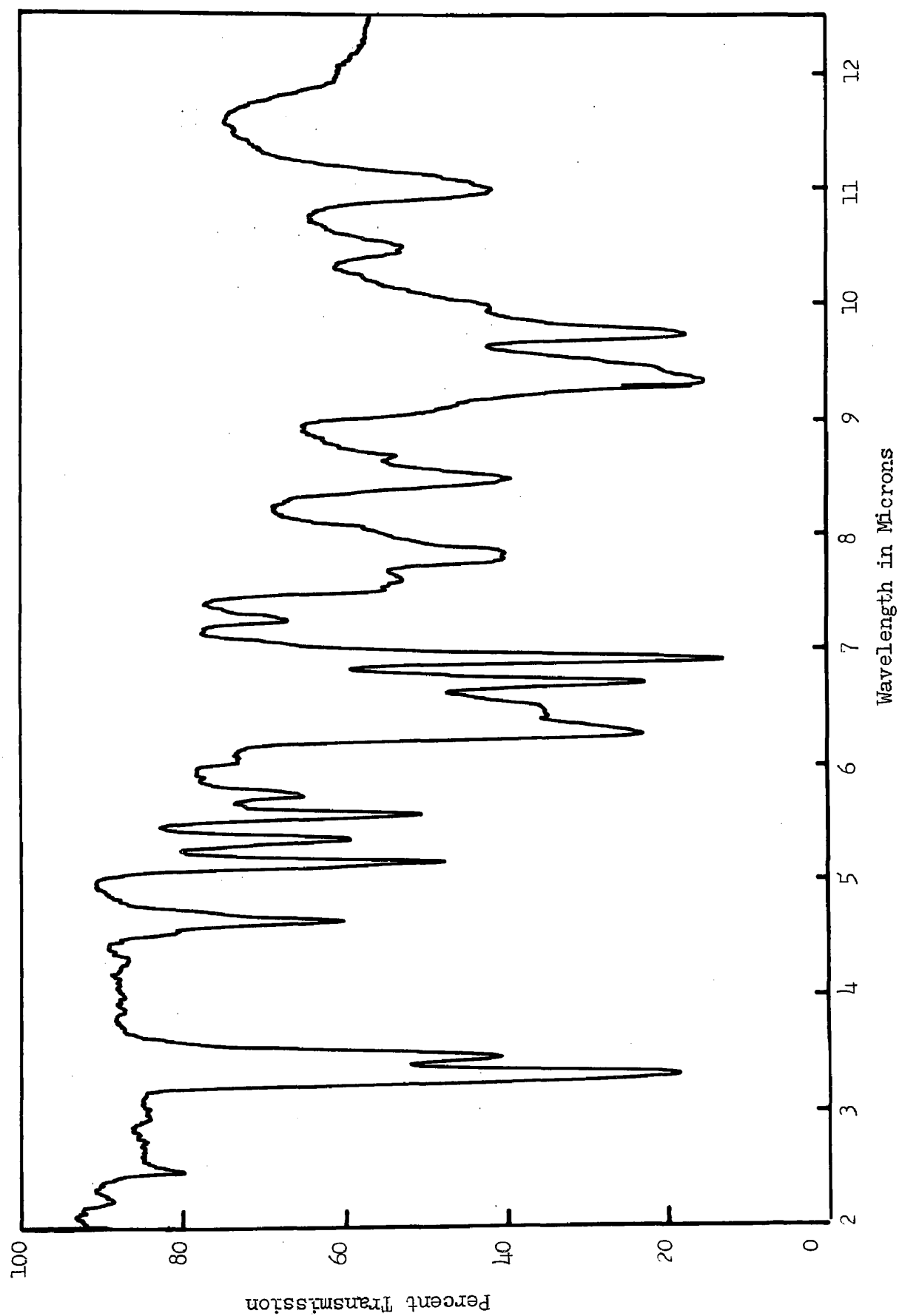


Figure 17. Infrared Spectrum of Diphenylmethane- d_4 (in Carbon Tetrachloride).

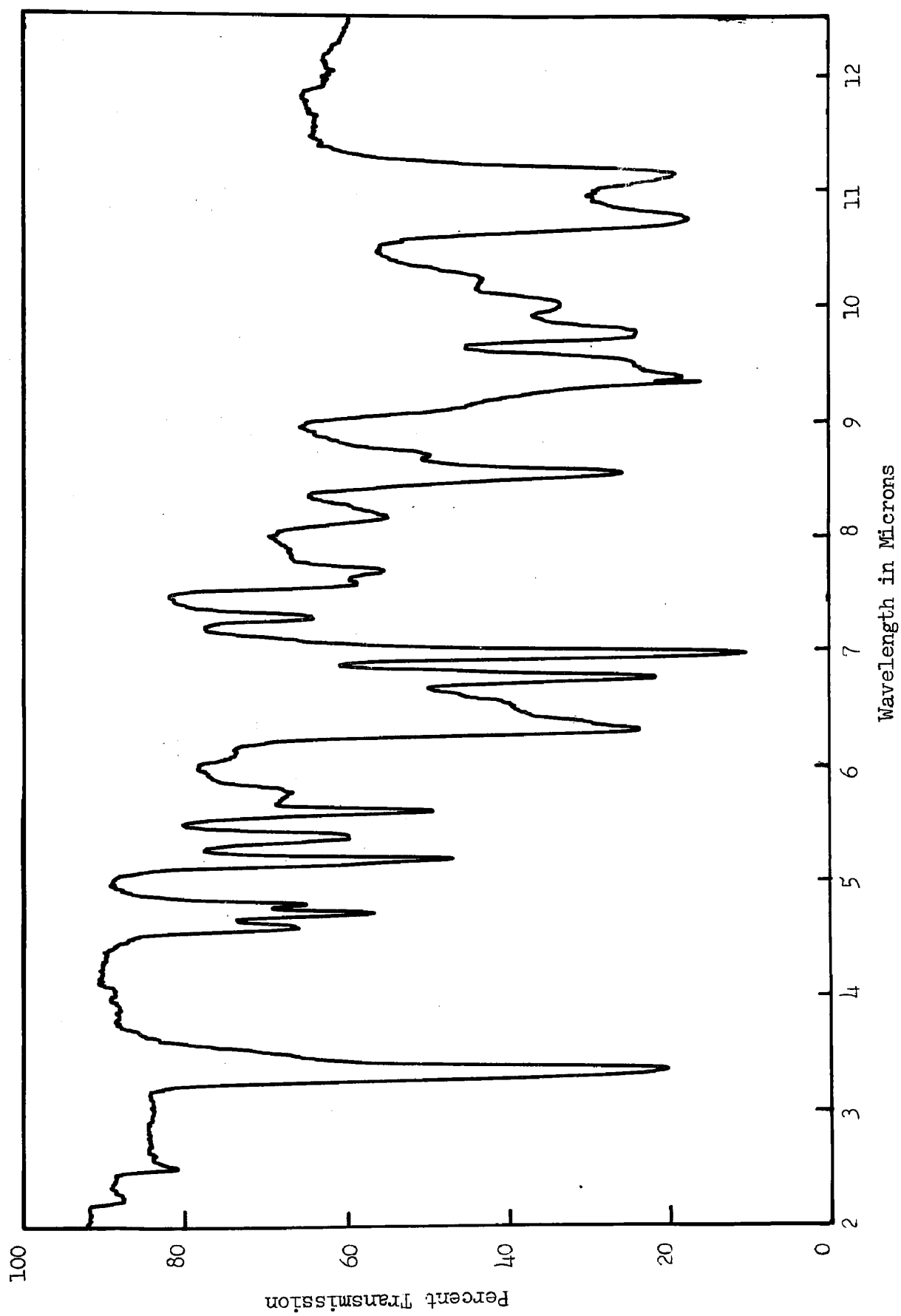


Figure 18. Infrared Spectrum of Diphenylmethane- d_8 , α (in Carbon Tetrachloride).

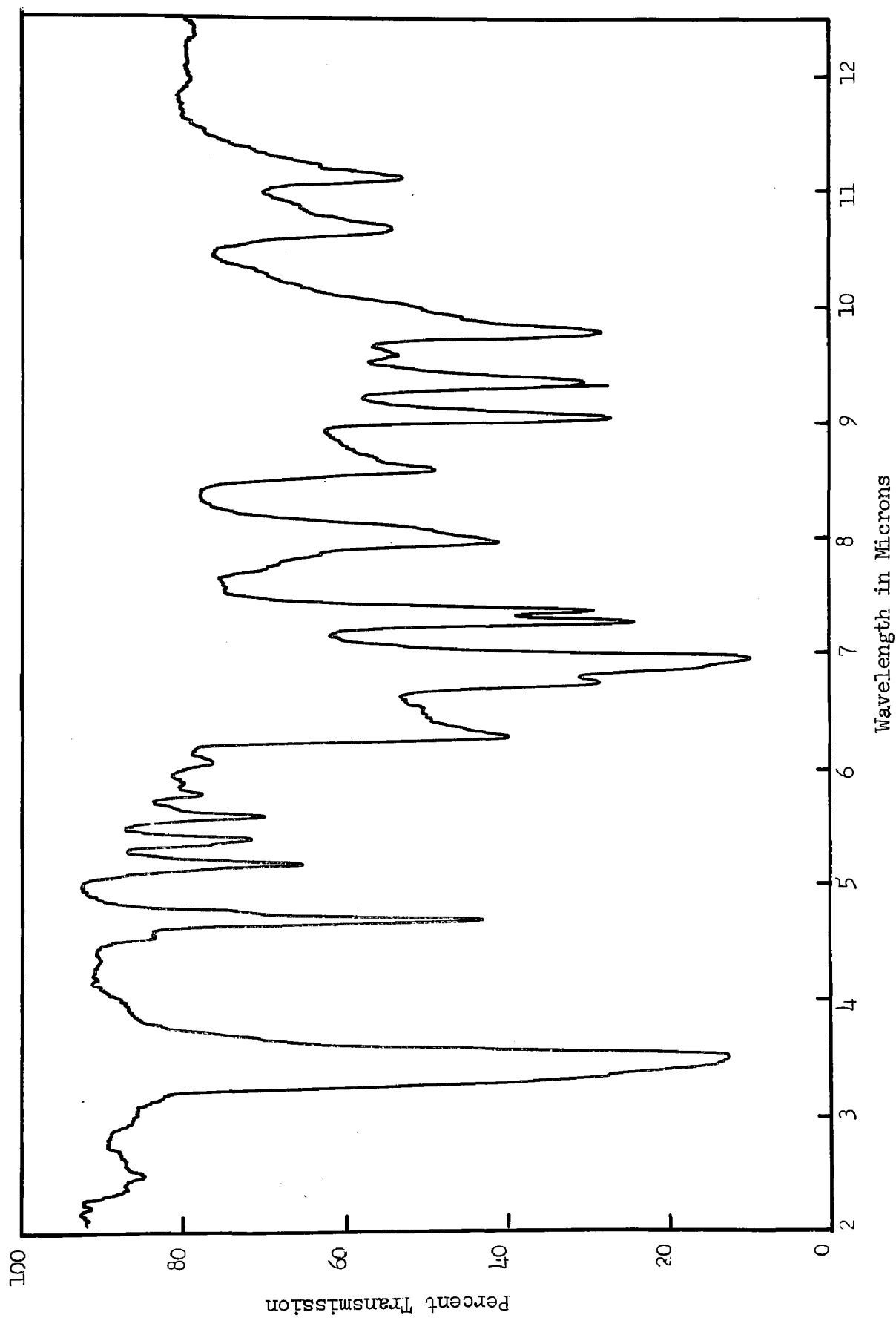


Figure 19. Infrared Spectrum of Cumene-d₉ (in Carbon Tetrachloride).

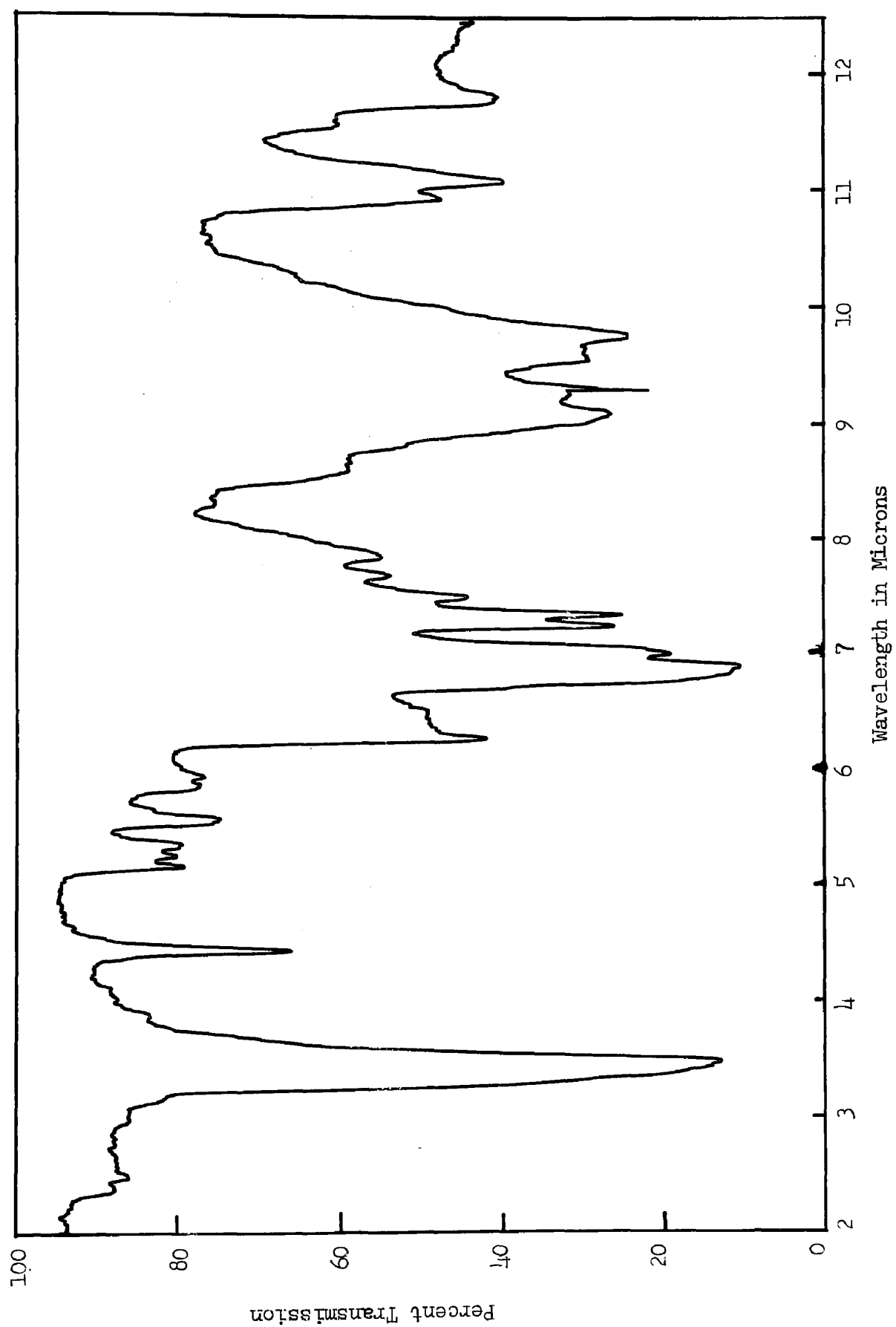


Figure 20. Infrared Spectrum of Cumene-d_p (in Carbon Tetrachloride).

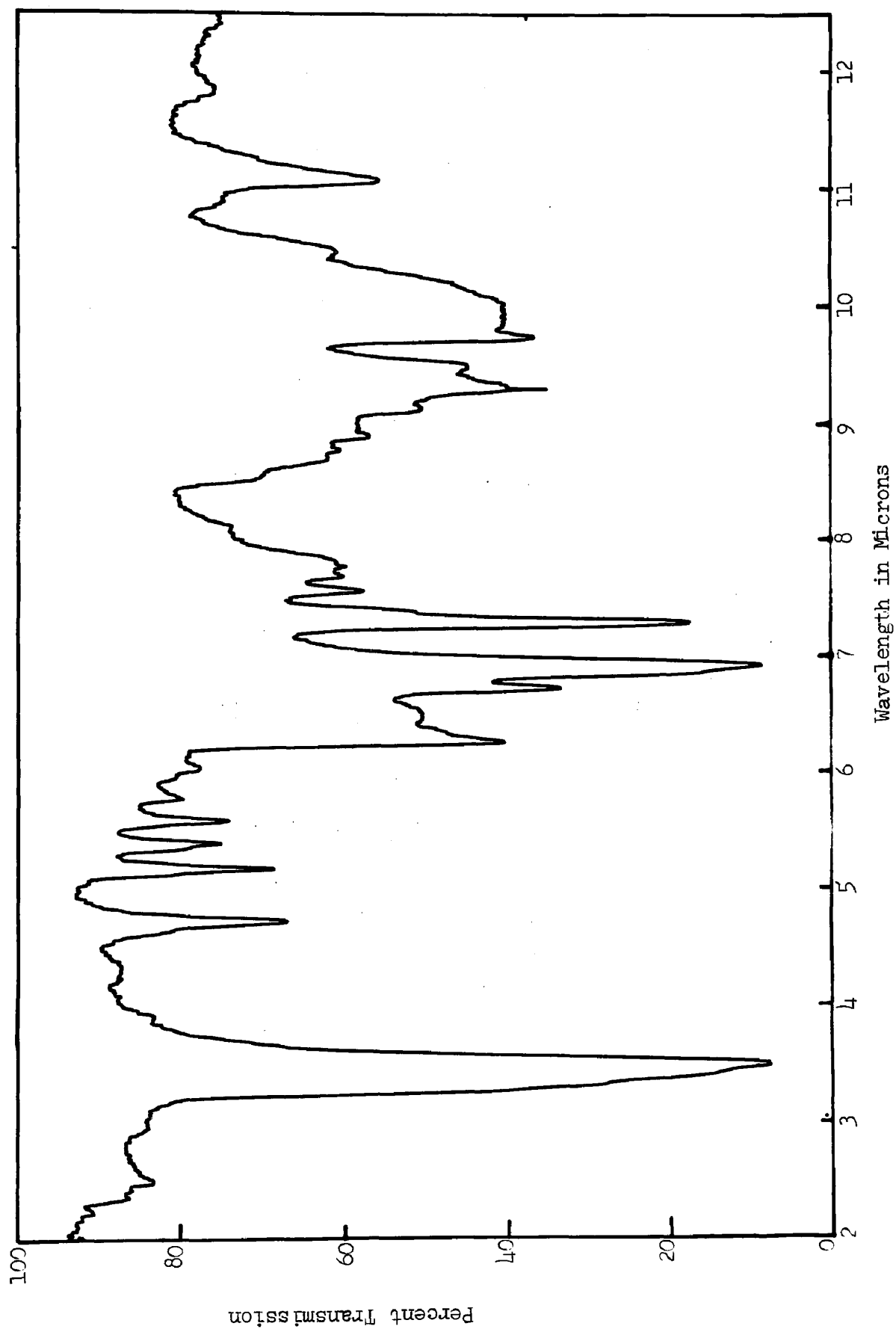


Figure 21. Infrared Spectrum of sec-Butylbenzene-d₉ (in Carbon Tetrachloride).

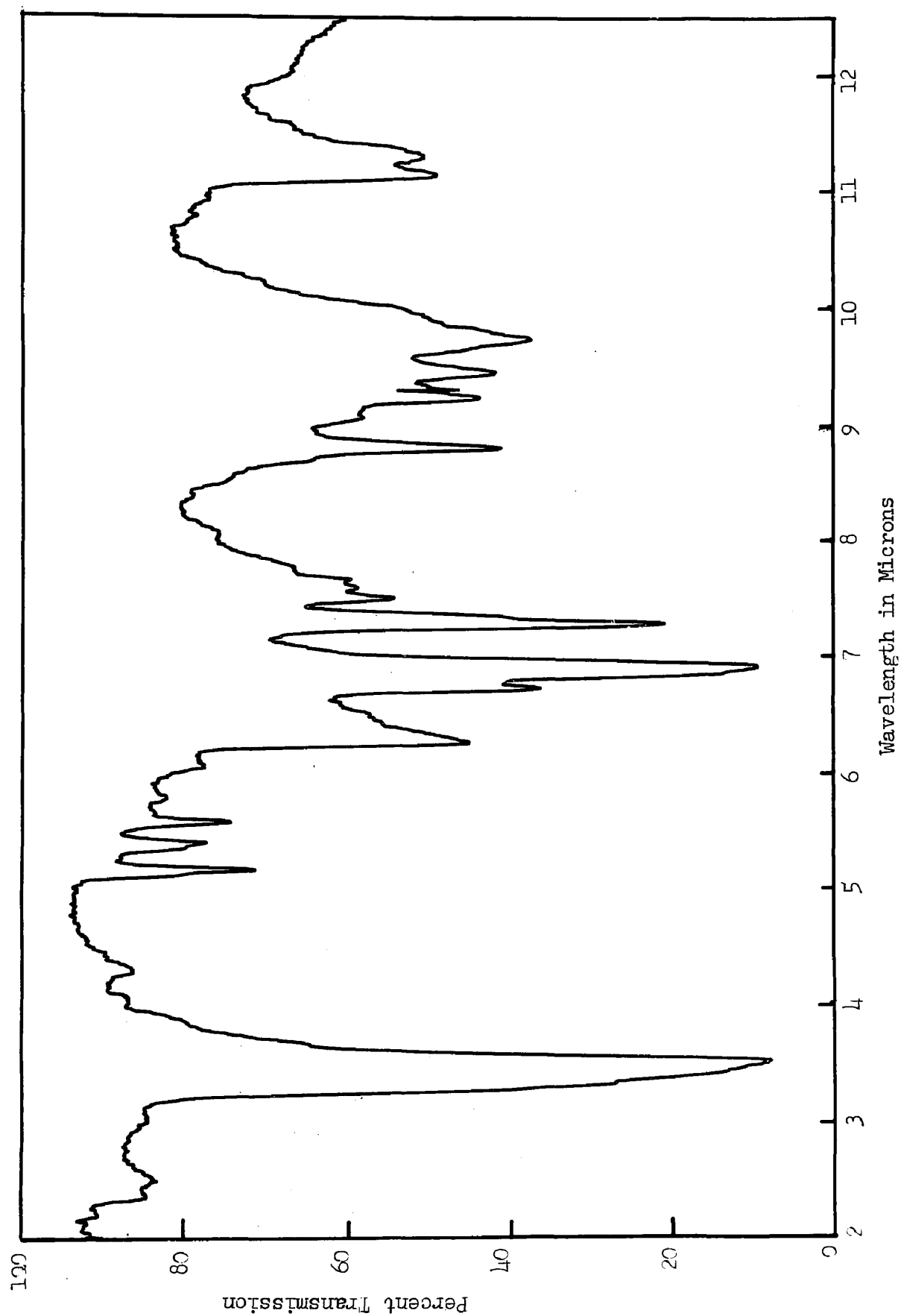


Figure 22. Infrared Spectrum of 3-Phenylpentane (in Carbon Tetrachloride).

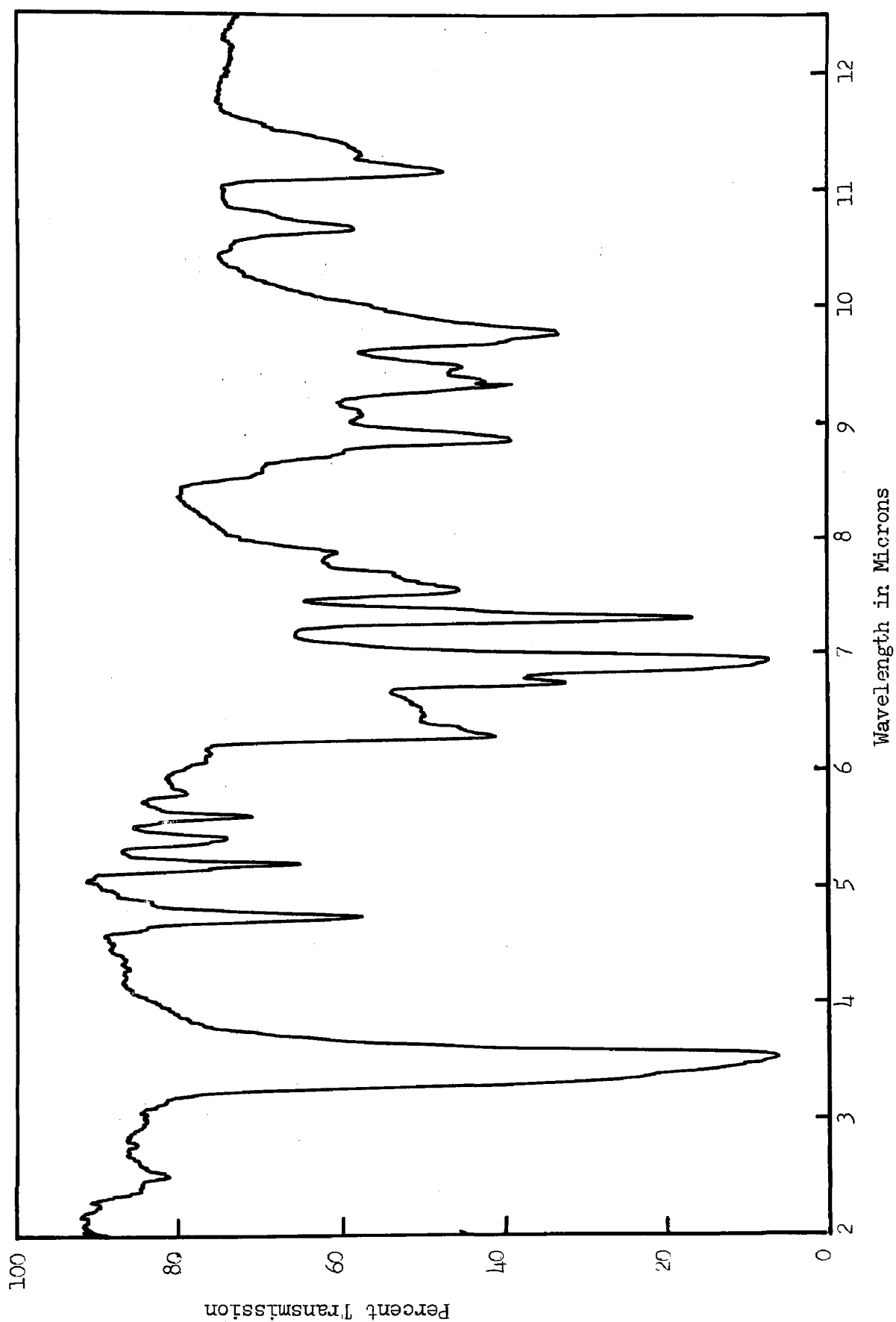


Figure 23. Infrared Spectrum of 3-Phenylpentane-d₈ (in Carbon Tetrachloride).

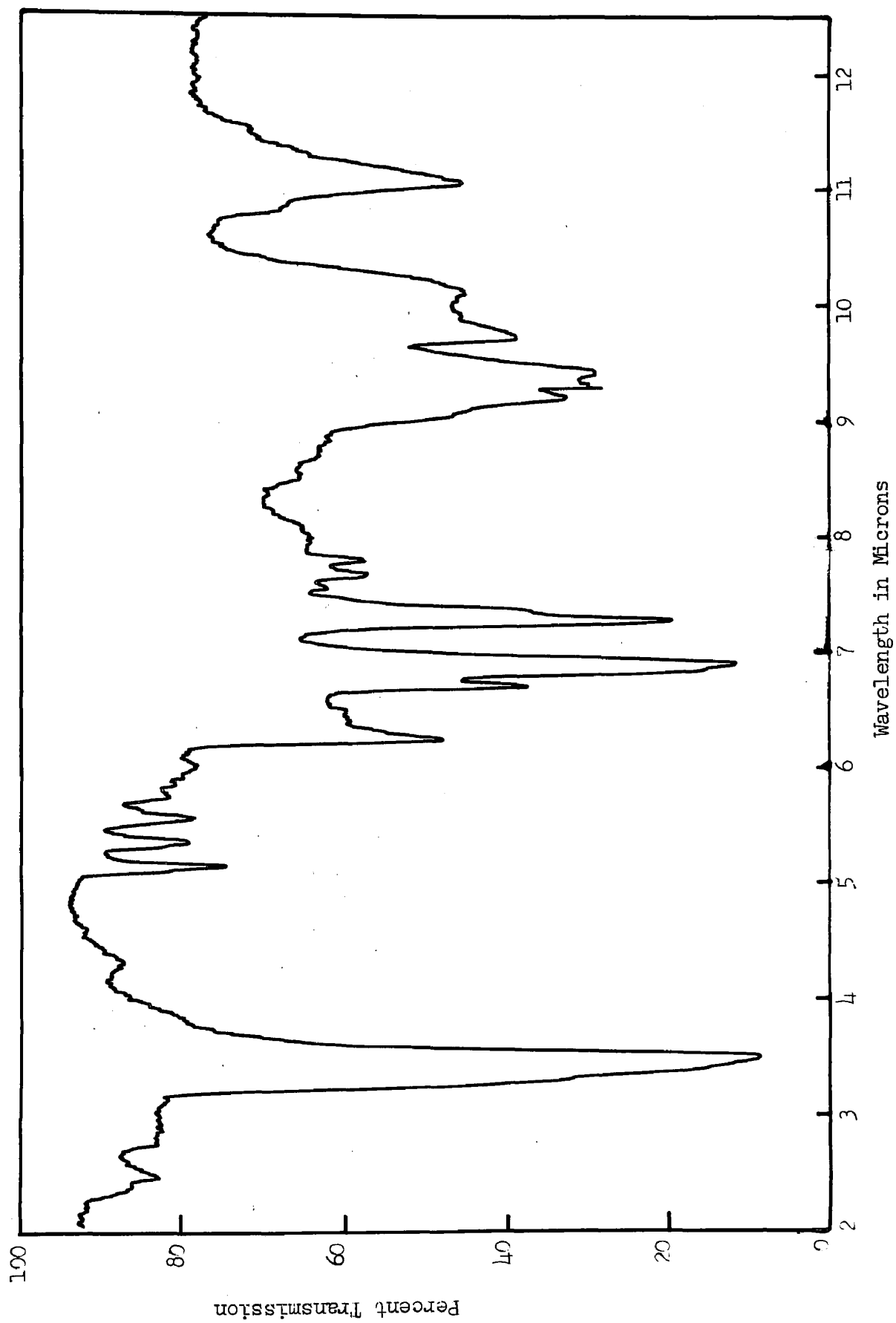


Figure 24. Infrared Spectrum of 2-Phenylpentane (in Carbon Tetrachloride).

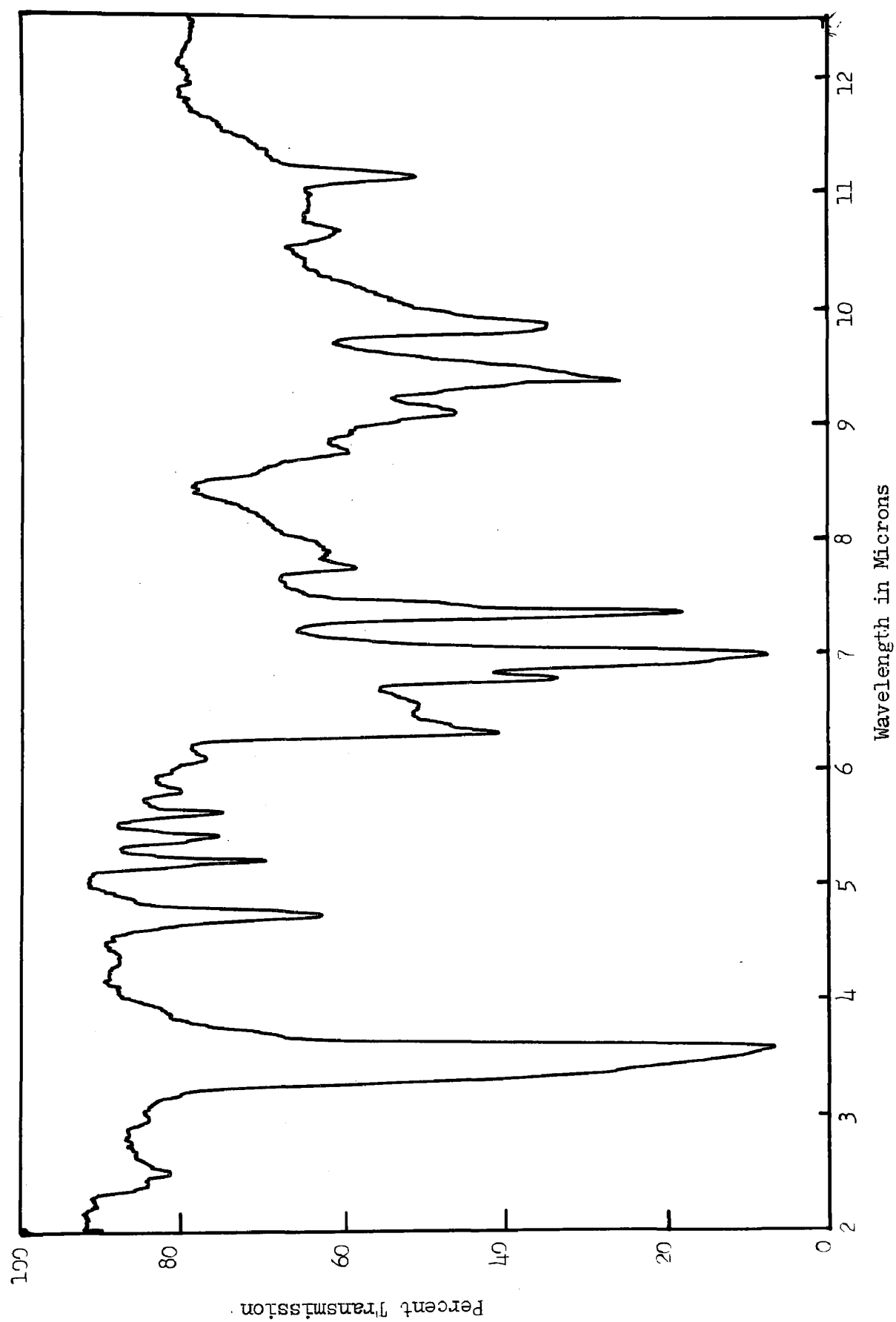


Figure 25. Infrared Spectrum of 2-Phenylpentane- d_4 (in Carbon Tetrachloride).

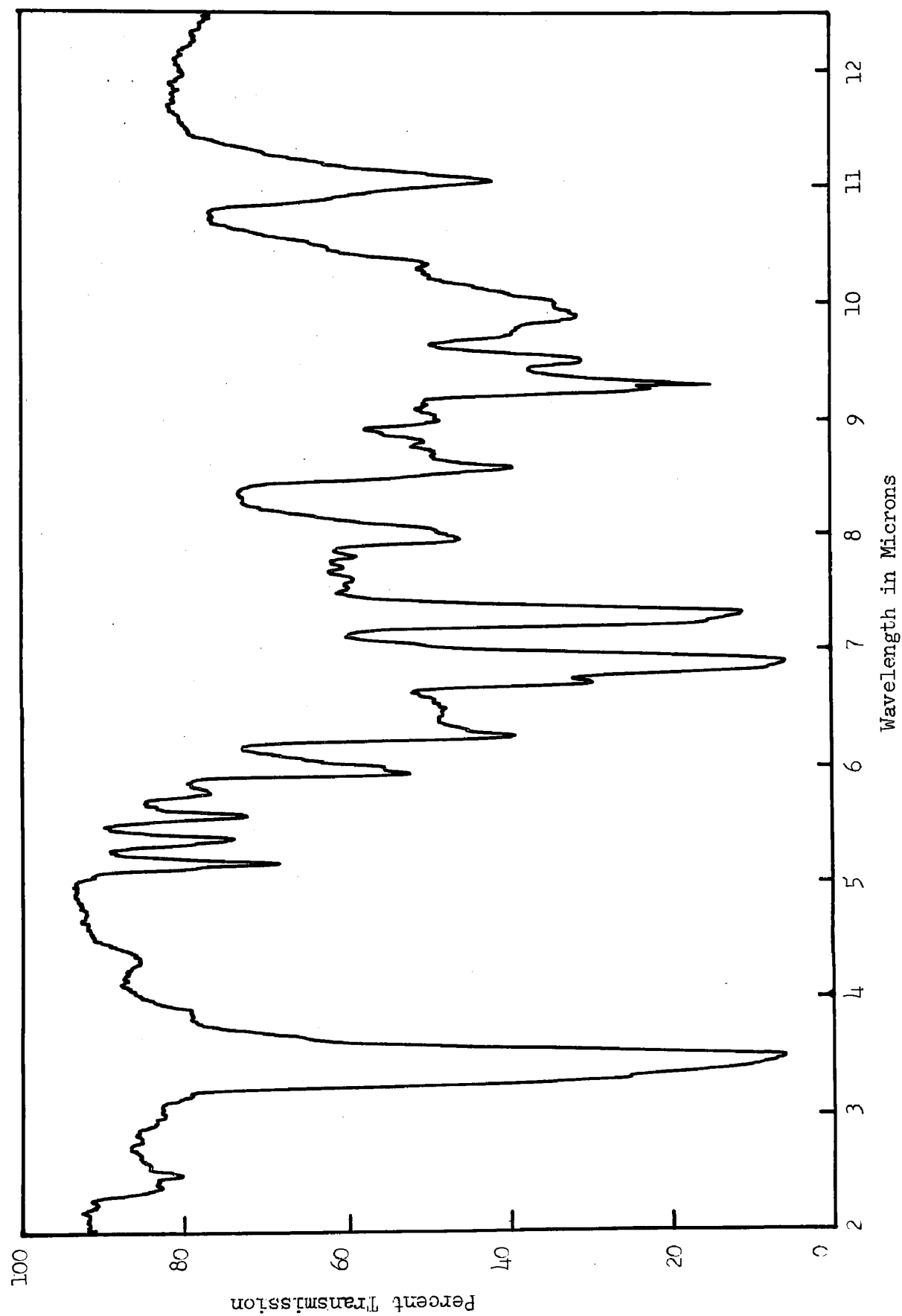


Figure 26. Infrared Spectrum of 2-Methyl-3-phenylbutane (in Carbon Tetrachloride).

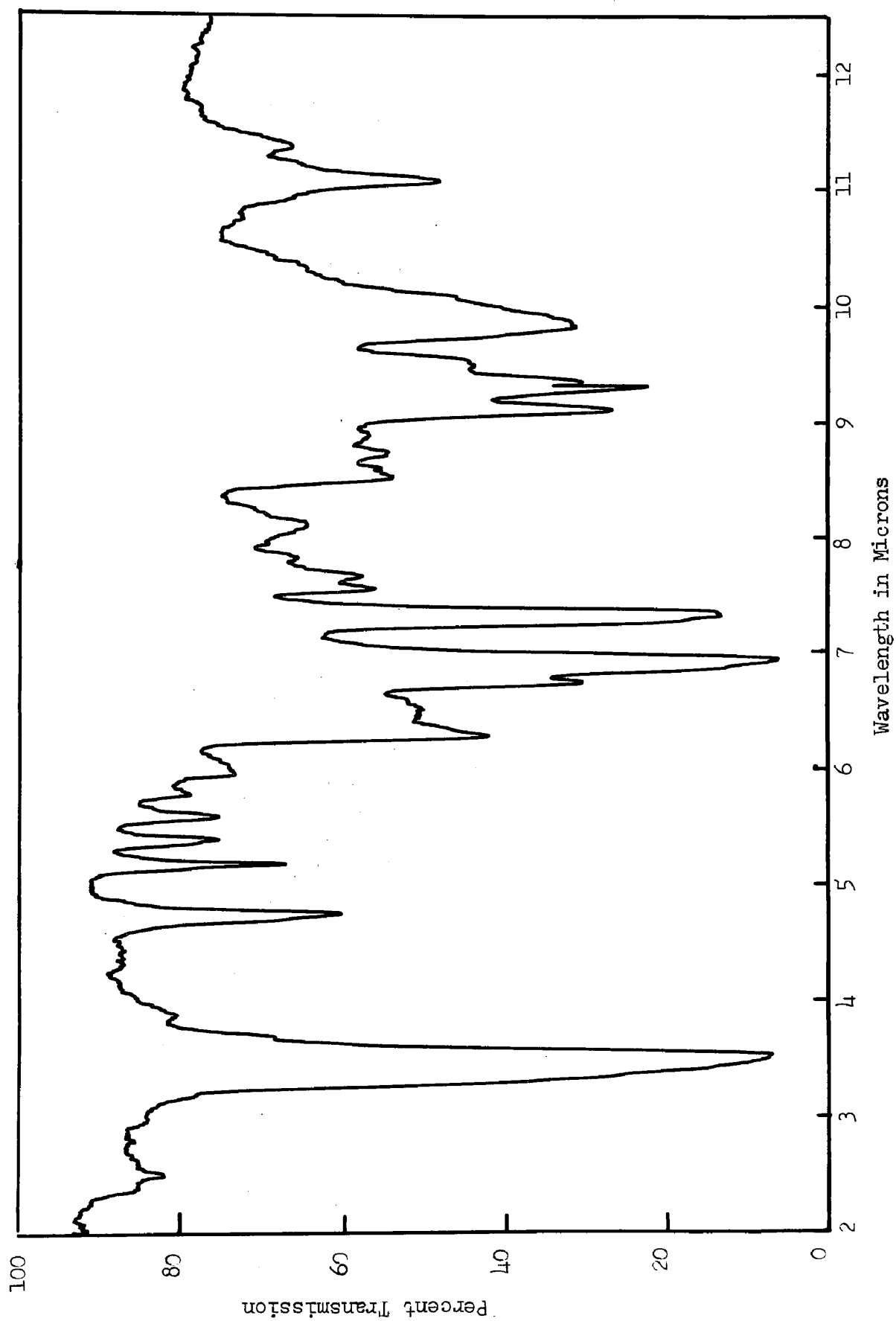


Figure 27. Infrared Spectrum of 2-Methyl-3-phenylbutane- d_4 (in Carbon Tetrachloride).

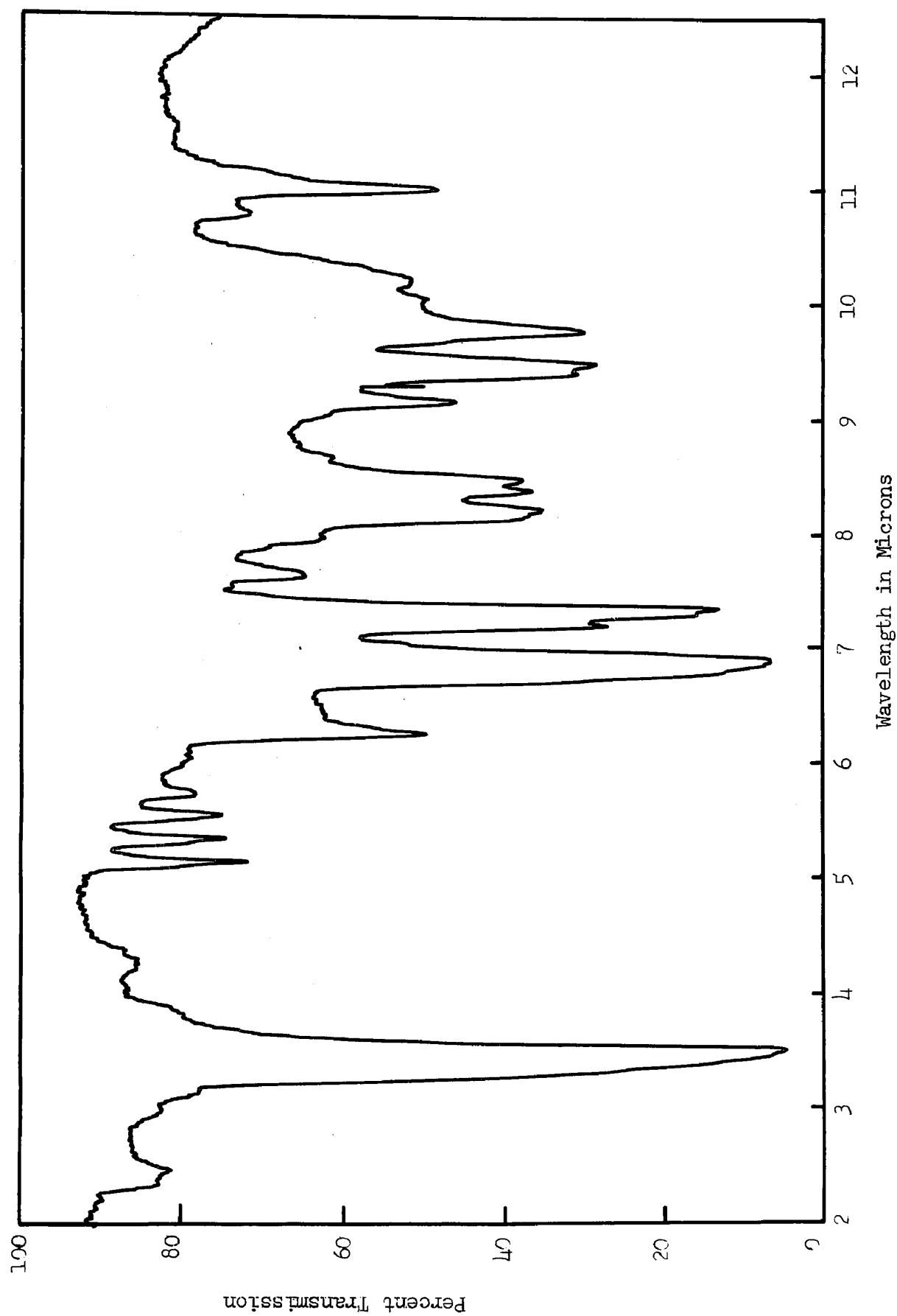


Figure 28. Infrared Spectrum of 2,2-Dimethyl-3-phenylbutane (in Carbon Tetrachloride).

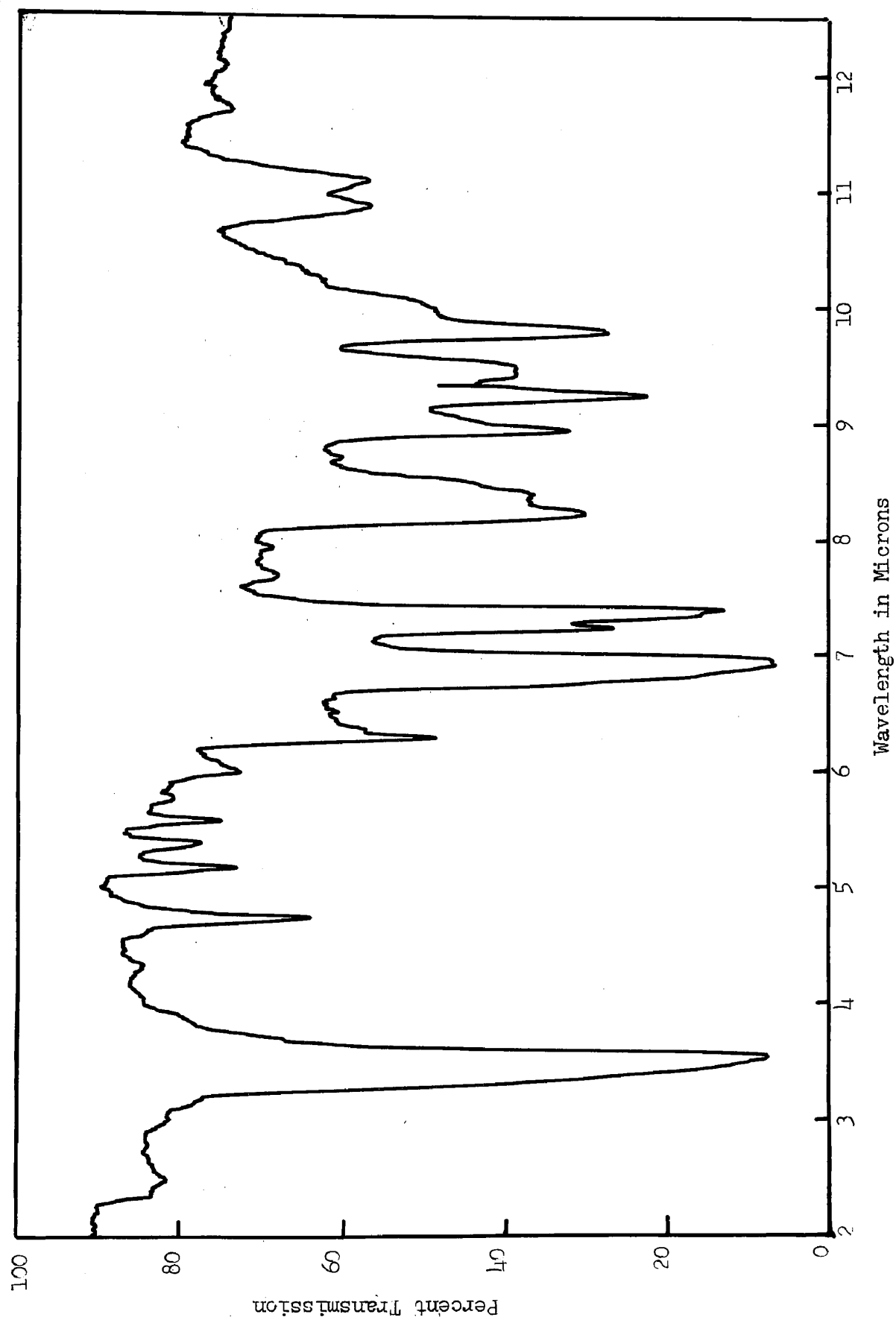


Figure 29. Infrared Spectrum of 2,2-Dimethyl-3-phenylbutane-d₉ (in Carbon Tetrachloride).