This is to certify that the

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Michael Tornaritis

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Major professor

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HYDRIDE TRANSFER REACTIONS

By

Michael Tornaritis

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ABSTRACT

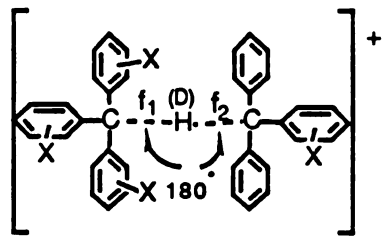
HYDRIDE TRANSFER REACTIONS

By

Michael Tornaritis

The purpose of this research was to examine the structure of the transition states of intermolecular hydride transfer reactions, i.e., whether they are linear or trigonal, by using as a probe hydrogen-deuterium kinetic isotope effects. Three sets of reactions were examined.

The first set involved reactions of triarylmethyl cations with triarylmethanes and their deuterated (at central carbon) analogs. These reactions, which are considered to be one-step hydride transfer reactions, gave $^{k}H/^{k}D$ isotope effects in the range 7-9. In view of the fact that the transition states are quite symmetrical with similar force constants f_1 and f_2, the large kinetic isotope effects exhibited by these reactions support a linear transition state (I).

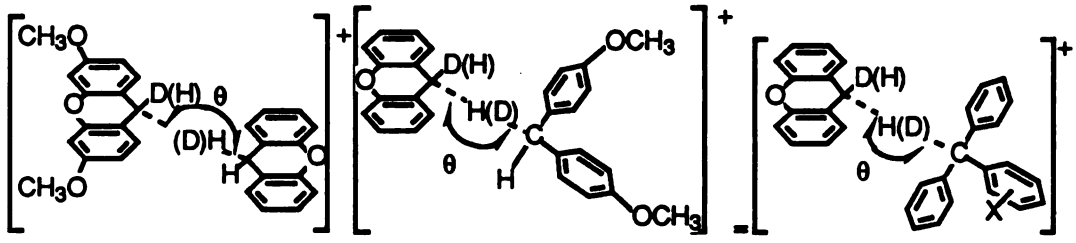


I

The data were not accurate enough to determine activation energy parameters and assess the extent of any mechanical tunneling.

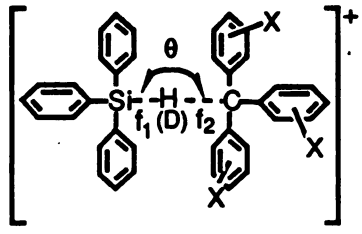
The second set of reactions involved the less sterically hindered xanthene system by reacting substituted xanthenes with the 9-xanthyl cation and xanthene with the diarylmethyl and triarylmethyl cations. The obtained $^{k}H/^{k}D$ kinetic isotope effects, 3.5-7.5, are consistent with transition states (II, III, IV) where the angle between

donor-hydrogen-acceptor is 120-150° on the assumption that the force constants on either side of the hydrogen are the same; it is also possible that the transition states are linear with somewhat unequal force constants on either side of the hydrogen



II III IV

The third set involved the reactions of triphenylsilane with triarylmethyl cations. No assessment of the structure of the transition states (V) of these reactions could be made because the kinetic isotope effects (1.6-2.2), which are in the range assigned by O'Ferral to cases where the angle between donor-hydrogen-acceptor is about 90°, may be due to the expected large differences in the force constants f_1 and f_2.



V

Our investigations showed that the only reacting center of the triarylmethyl cations is the central carbon atom. No hydride attack on the aryl rings, followed by hydrogen rearrangement to the central methine carbon, was detected. Similar conclusions were drawn from our studies with the 9-xanthyl, 2,6-dimethoxy-9-xanthyl and dianisylmethyl cations.

The identity reaction between the triphenylmethyl cation and triphenylmethane was found to be appreciably slower than the corresponding reaction of xanthene with the 9-xanthyl cation.

TO MY FAMILY

ACKNOWLEDGEMENTS

To my father I own
the life of to my teacher
the enlightened life.
Alexander the Great

I would like to express my deep appreciation to my advisor, Professor G.J. Karabatsos, for his guidance, encouragement and friendship.

My thanks are also extended to the Department of Chemistry at Michigan State University including both faculty and staff. Financial support provided by the department is gratefully acknowledged.

You understand who your
true friend is when you
are in need and danger.
Ancient Greek proverb

I will always remember my friends and co-workers including Asaad Salehi, A. Analyti, D. Voyiotzoylou, M. Kondylis and W. Park as well as the the Greek and Cypriot Student Association and the Greek American Community for their friendship.

Worship your Father
and Mother
Bible

Finally, I dedicate this work to my family for their continuous love and support.

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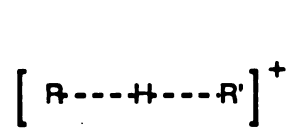
CHAPTER I

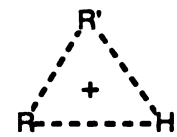
INTRODUCTION

INTRODUCTION

Reactions involving hydride transfers are quite common, and include not only those of academic interest but also several carried out on an industrial scale e.g., the catalytic cracking of hydrocarbons, as well as some biochemical reactions such as the reversible oxidation of alcohols to aldehydes and ketones by the use of alcohol dehydrogenases and $NAD^+(P)$-NAD(P)H coenzymes. The purpose of the research described in this thesis was to probe the structure of the transition states that involve hydride transfer, i.e., where they are linear (I) or trigonal II.



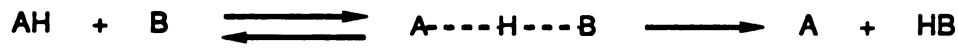
I



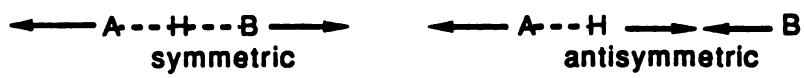
II

Before focusing on hydride transfers, however, a brief review of what is known about hydrogen transfers in general (proton, hydrogen atom, hydride) will be given.

Before 1960 the hydrogen atom or ion which was transferred from a donor to an acceptor was treated as a free species. For simplicity, this species was disassociated from the donor and associated with the acceptor in a two-center type reaction. In 1960 Westheimer[1] and Melander[2] separately introduced the three-center type transition state in a linear conformation for intermolecular transfers of a hydrogen atom or an ion. Westheimer's suggestion for this transition state resulted from the theoretical treatment of the reaction:

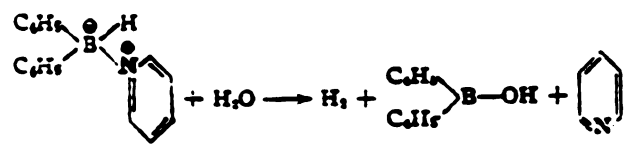


For the linear transition state A····H····B of this reaction he took into account only the symmetric and antisymmetric stretching vibrations in his calculations of deuterium kinetic isotope effect,



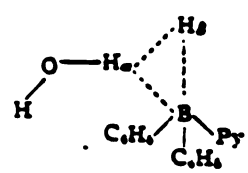
and ignored the bending vibrations and the structures of the A and B groups. Westheimer concluded that this linear transition state was the one which imposed the lowest energy and the minimum of steric interactions. Melander's suggestion of this same transition state resulted from the theoretical treatment of the shape of the landscape as a whole for the above reaction and is equivalent to that of Westheimer's.

The first suggestion of a nonlinear transition state for hydride transfer processes was made by Hawthorne and Lewis[3]. They suggested that "the only reasonable point of attack of an electrophile on a bond to hydrogen must be the center of high electron density, that is, the bond, and a linear configuration A----H----B is not to be expected." They based their suggestion on kinetic studies of the hydrolysis of pyridine diphenylborane



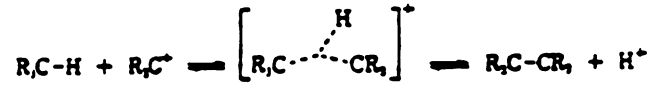
Hydrolysis of pyridine diphenylborane

Hawthorne and Lewis proposed the following transition state for the BH bond hydrolysis and



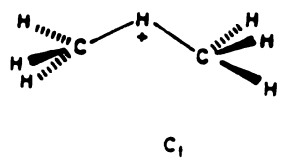
suggested an electrophilic attack on the high electron density BH_β bond from the electron poor side of the H_a, which is the opposite side of the oxygen. The possibility of all three atoms using the pair of electrons is shown by the dotted lines. Also, they suggested that the trigonal transition state may be general for hydrogen transfers.

The non-linear transition state in intermolecular hydride transfer reactions was favored also by Olah, who studied[4] the hydride abstraction from alkanes by using alkylfluoroantimonates. Working with superacid solvent systems, he was able to study stable carbocations and their reactions. He suggested for these reactions the three-center bonded pentacoordinated carbonium ion transition state,

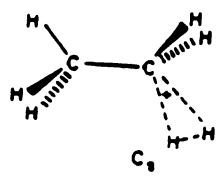


especially in tetriary-tetriary systems where the highly unsymmetric bridged carbonium ion minimizes the steric interactions. Olah based his conclusions on the relative composition of the product mixtures which were determined by gas chromatography, mass spectrometry and NMR spectroscopy. He emphasized, however, that due to the complexity of the systems, small changes in conditions may differentiate the composition of the product mixtures.

A non-linear structure for C--H--C was proposed[5] by Raghavachari, Whiteside, Pople and Schleyer for protonated ethane, $C_2H_7^+$. According to their theoretical calculations, which were carried out an optimized HF/6-31 G* level, the lowest energy structure, C_1, which is shown below,



C_1

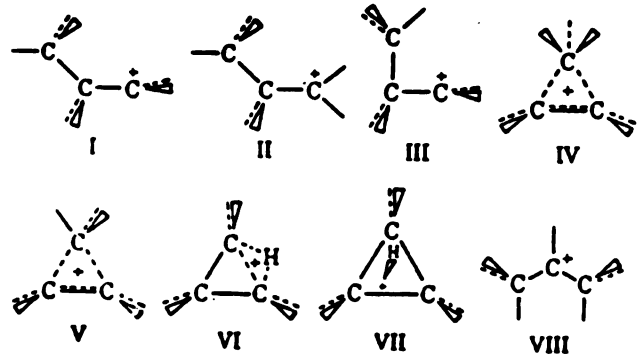


C_s

"is strongly distorted from a D_{3d} structure with an angle CH_1C of 121.7°. It is also twisted by about 30° from a staggered C_s configuration."

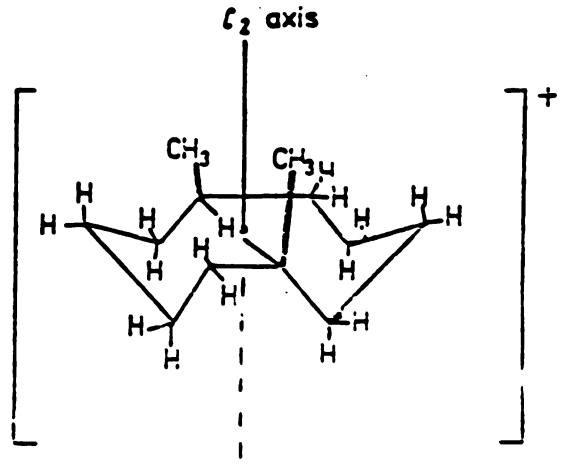
The transition states of intramolecular 1,2-hydride rearrangments are by necessity non-linear. Intramolecular-hydride rearrangements may occur from one

carbocation to a slightly less stable carbocation, whenever there is no other rapid reaction for the former cation to undergo, and the energy barrier to rearrangement is relatively low. Examples for these rearrangements are those occurring in the propyl cation. The low temperature NMR spectra of the propyl $C_3H_7^+$ in superacid medium show hydrogen and carbon scrambling.[6] The superacid medium eliminates other reactions that would compete with the hydride rearrangements. The transition states for these rearrangements have been calculated from detailed molecular orbital calculations for the $C_3H_7^+$ by Pople, Schleyer and co-workers,[7] using STO-3G,4-31G and 6-31G sets. The structures examined were I-VIII.



The calculations predict VI to be a transition state, whereas VII, which lies at an energy minimum, is an intermediate. Because of the special contraints imposed by the system the transition state VI is by necessity nonlinear.

More examples of intramolecular hydride transformations are the hydride shifts which are facile in C_8-C_{11} sized rings in superacid medium. The geometry of the ring forces the hydride nearby the empty p orbital to bridge with it. This is exemplified in the ^1H and ^{13}C NMR studies by Sorenson and Kirchen[8] for the 1,6-dimethyl-cyclodecyl cation which proved to exist in a symmetrical μ-hydrido 1,6-hydrogen-bridged structure:



The strainless cis-decalin geometry is depicted, which shows no deviation from linearity of the C-H-C angle. Some bending, however, which would improve the cis-decalin type conformation, would be expected.

The deuterium kinetic isotope effect has been used extensively for the determination of the mechanisms of chemical reactions. The theory of the magnitude of this effect is very well established.

For the reaction mentioned previously

$$AH(D) + B \rightleftharpoons A\cdots H(D)\cdots B \longrightarrow A + (D)HB$$

Westheimer[1] states that "the major portion of the kinetic isotope effect arises from contribution to the activation energy from changes in zero-point energy which occur when the reactants are converted to an activated complex." Using the stretching vibration frequency for hydrogen and deuterium he calculated the activation energies for the above reaction and thus the difference in the zero-point energies of the hydrogen and deuterium species to be 1.15 kcal/mol at 300°K. This corresponds to a factor of 7 for the isotope effect. He assigned this magnitude of the isotope effect for a linear transition state.

For many reactions, especially those involving intramolecular hydrogen transfer, the transition state is not linear. O'Ferral[9] calculated the effect of such a geometric

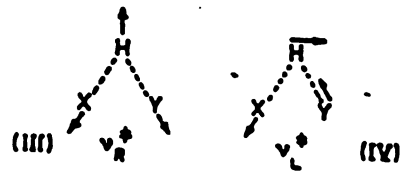
change upon the magnitude of $^{k}H/^{k}D$ at 25°C. He considered for his studies a model which involved a minimum of five atoms. This model is shown below along with the force constants that have been used in the calculations:

The maximum isotope effect is expected in a linear transition state (I,II) when the force

(I) $\overleftarrow{X}\cdots H\cdots\overrightarrow{Y}$ ν_R:

(II) $\overleftarrow{X}\cdots\overrightarrow{H}\cdots\overleftarrow{Y}$ ν_L:

constants on either side of the hydrogen are the same and thus there is a balance of force on it (no motion of H in the symmetric stretch). In a nonlinear transition state (III,IV) the balance does not exist and a smaller isotope effect is expected. "(i) By assuming a reasonable



dependence on transition state structure, as expressed by the order, x, of the bond to hydrogen being broken, and (ii) by supposing that in the limit x⟶ 0 or 1, force constants in the transition state reduce to their corresponding values in reactants and products," O'Ferrall concludes: "For the linear transition state (β-180°), the isotope effect showed the normal dependence on x, with $^{k}H/^{k}D$ approaching unit as x⟶ 0 or 1 and at a maximum for x = 0.5. For the most extreme non-linear cases, with β=60° or 90°, the dependence of $^{k}H/^{k}D$ upon x was much less marked and for no value of x did the isotope effect depart substantially from unity. For larger angles, β=120° or 150°, behavior intermediate between that for the linear and extreme non-linear transition states was found." These results can be represented by Figure 1.

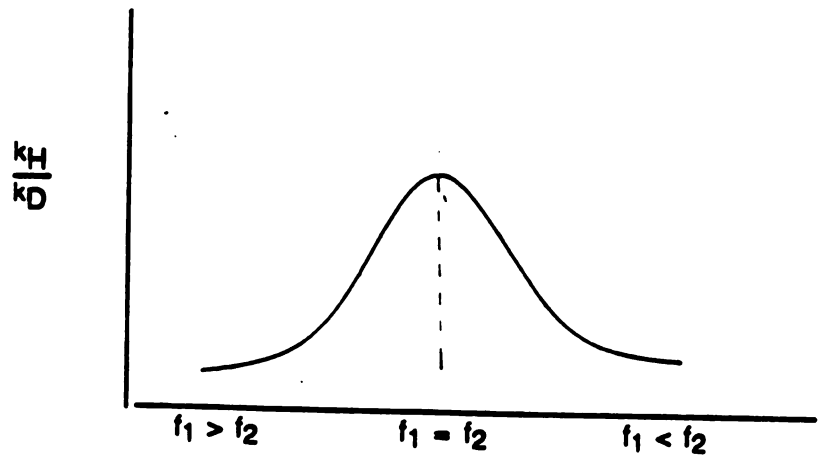


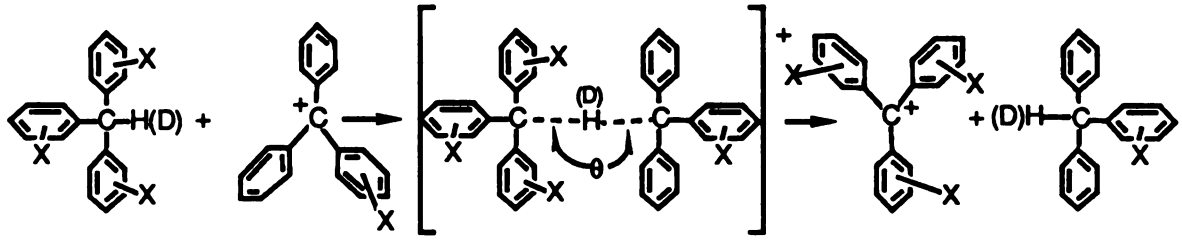
Figure 1. Schematic representation of the isotope effect versus the force constants in either side of the hydrogen.

In terms of numbers the maximum isotope effect of a linear transition state is about 7.9. This value is not significantly affected by small deviations from linearity. For a 150° angle, however, between donor-hydrogen-acceptor the isotope effect is reduced to 6.2-6.4; for a 120° angle to 3.0-3.9; and for a 90° angle to 1.7-2.3.

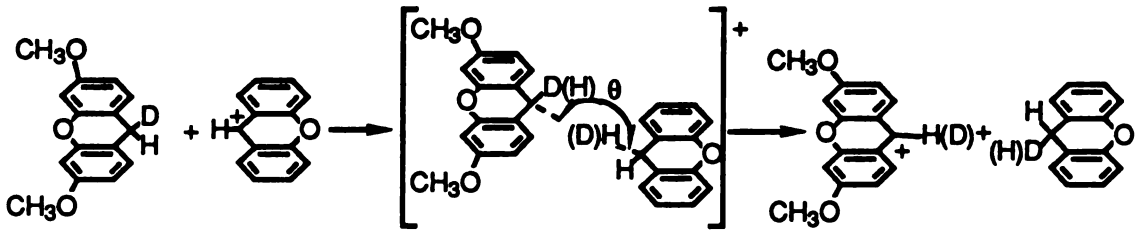
Isotope effects involving hydride transfers are small. For example, the isotope effect for the previously mentioned[3] hydrolysis of pyridine diphenylborane, was found by Hawthorne and Lewis to be 1.52. Also, according to Bartlett's and Collum's findings[10] the $^kH/^kD$ for the oxidation of isopropyl alcohol by the triphenylmethyl cation was 1.8-2.6. These small isotope effects may arise either because the transition states are nonlinear or because the systems used lie on the low left side of the curve of the Figure 1.

Our studies were designed to establish the nature of the transition states in intermolecular hydride transfer reactions by examining the kinetic isotope effects of three sets of reactions. The first set involves the reactions of triarylmethyl cations and triarylmethanes. This system, because of the symmetrical force constants on either side of the hydrogen falls at the top of the curve of the Figure 1. Therefore, the only factor

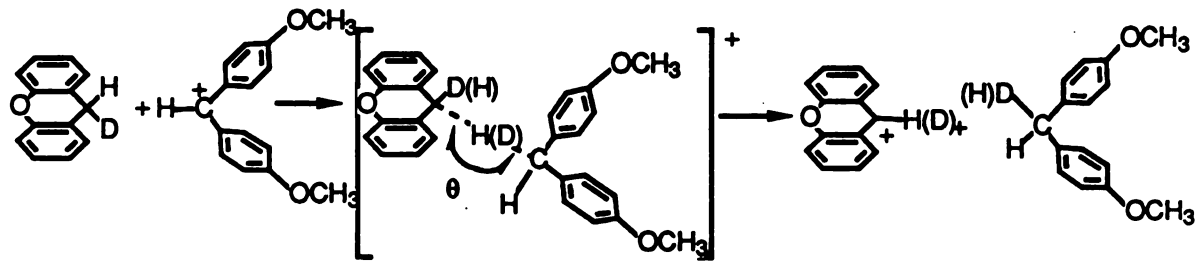
(other than tunneling) controlling the magnitude of the isotope effect is the angle θ between donor-hydrogen-acceptor.



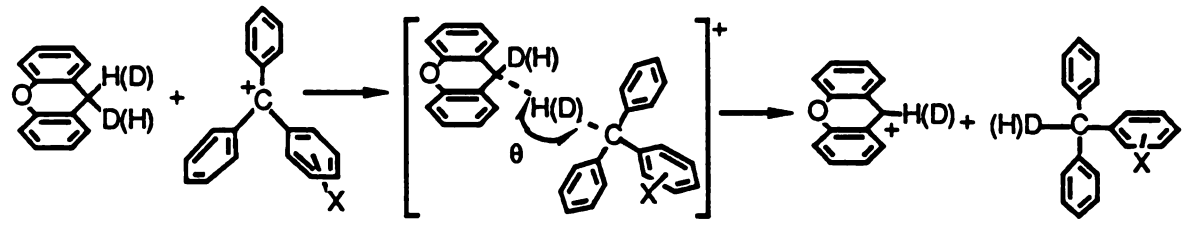
The second set involves the less sterically hindered xanthene system reacting with substituted xanthenes, and with dianisyl and triaryl compounds. These systems would lie at the top (xanthene-xanthene)



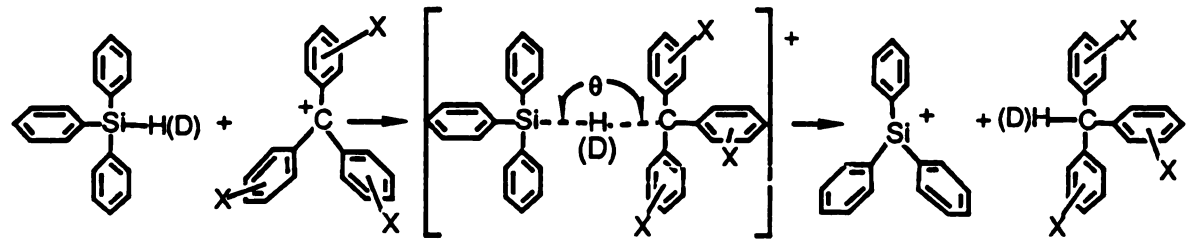
and the left side of the curve of Figure 1, (xanthene-dianisyl,



xanthene-triaryl)



The kinetic isotope effect, - - except for the xanthene reaction - - would thus depend not only on θ, but also on the relative magnitudes of f_1 and f_2. The third set involves the reactions of triphenylsilane with the triarylmethyl cations.



This system most likely would lie at the left low side of the curve of the Figure 1.

CHAPTER II

TRIARYLMETHYL CATIONS REACTIONS

EXPERIMENTAL

I. Preparations

Triphenylmethane enriched by 50% C-13 at the methine carbon:

The title compound was prepared according to the following procedure. Barium carbonate (3.2 gr), 50% enriched in C-13, was placed in a 50ml three-necked round-bottomed flask of the apparatus depicted in Figure (1).

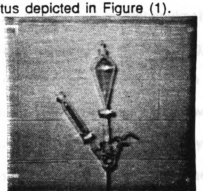


Figure 1. Apparatus used for the preparation of $^{13}CO_2$

After the air of the system was evacuated, (concentrated) sulfuric acid was added dropwise to the barium carbonate. Ninety percent of the three-necked round-bottomed flask was filled with sulfuric acid, its contents were stirred, and finally the solution was warmed at 45°C for about 10 minutes. The stopcock of the 500 ml separator funnel was closed and the produced carbon dioxide was trapped in the funnel. The separator funnel then was connected with a 500 ml round-bottomed flask containing phenylmagnesium bromide (2.94 g) in ether (60 ml). The carbon dioxide slowly and cautiously, because of the closed system and the exothermicity of the reaction, was allowed to react with the Grignard reagent. The solution was shaken for 10 more minutes and then was hydrolyzed with saturated ammonium chloride. The ether layer was separated and dried over sodium sulfate and after distillation of the ether, benzoic acid was obtained. The overall yield of the benzoic acid formed was 76%. Following basically the procedure of Ray, Kurland and

Colter[11] for the preparation of carbinols, the benzoic acid was refluxed overnight with ethanol in the presence of sulfuric acid to form the ethyl ester (95% yield).

The ethyl benzoate (1.46 g) was reacted with phenylmagnesium bromide (4.4 g) to produce triphenylmethanol. Treatment of the carbinol with acetyl chloride according to the procedure of Bachmann[12] gave triphenylmethylchloride, which upon reduction with excess lithium aluminum hydride led to triphenylmethane enriched by 50% C-13 at position 1. For the reduction reaction, the chloride (1 g) was dissolved in benzene or ether (30 ml) in a 100 ml round-bottomed flask and the lithium aluminum hydride (about 0.1 g) was added slowly . The reaction mixture was stirred, refluxed overnight, and the excess lithium aluminum hydride was destroyed by addition of water. The organic layer was separated, dried over sodium sulfate, and after distillation of the solvent gave triphenylmethane. The NMR spectrum of the product in acetonitrile is shown in spectrum 21.

Trianisylmethane:

The trianisylmethanol for the preparation of the title compound was prepared following the procedure of Ray, Kurland and Colter.[11] For this, anisyl acid was treated with methanol in the presence of sulfuric acid to form methylanisate. The ester was reacted with 4-methoxyphenylmagnesium bromide to produce trianisylmethanol.[11,13] This carbinol also was produced by the reaction of excess 4-methoxyphenylmagnesium bromide (3.5 times) with diethylcarbonate. The crude product was purified by formation of the picrate. For this to the hot solution of trianisylmethanol (7 g) in ethanol (50 ml) was added with stirring picric acid (7 g). The solution was cooled in an ice bath and the red complex which precipitated was filtered and washed with methanol. The complex was dissolved in benzene and was extracted with 5% sodium hydroxide solution until the yellow petals which were formed with the addition of the sodium hydroxide were dissolved. Then the organic layer was separated and was dried over

sodium sulfate. After evaporation of the solvent trianisylmethanol was obtained as a red oil. This carbinol was treated with acetyl chloride to prepare of trianisylmethyl chloride, which was then reduced by lithium aluminum hydride or lithium aluminum deuteride to give trianisylmethane, or deuterated trianisylmethane. The reduction procedure was the same as that used to prepare triphenylmethane. The trianisylmethanes were recrystallized from ethanol. The acetonitrile solutions of the trianisylmethane gave spectrum 2.

Tri-p-tolylmethane:

The tri-p-tolylmethane was prepared according to the procedure described by Newman and Deno.[14] Diethylcarbonate was reacted with p-tolylmagnesium bromide to give tri-p-tolylcarbinol, which when treated with acetyl chloride, gave tri-p-tolylmethyl chloride. Reduction of the chloride with lithium aluminum hydride or lithium aluminum deuteride gave tri-p-tolylmethane or deuterated tri-p-tolylmethane.

Anisyldiphenylmethyl cation[15]:

The carbinol needed for the preparation of the title cation was synthesized according to the general procedure of Ray, Kurland, and Colter[11] for the preparation of carbinols from benzophenone and Grignard reagents. To a solution of benzophenone in ether, was added excess 4-methoxyphenylmagnesium to produce anisyldiphenylmethanol.[13] This carbinol (4 g) was dissolved in propionic anhydride (37 ml) and the solution was cooled in ice. When tetrafluoroboric acid (3.65 ml, 48% aqueous solution) was addded dropwise, solid anisyldiphenylmethyl tetrafluoroborate was precipitated. The cation was filtered under argon and was washed with cooled petroleum ether. The acetonitrile solution of this cation gave spectrum 15.

II. Reactions studied

Reaction of Trianisylmethane with Triphenylmethyl Tetrafluoroborate (spectra 1-12):

(1) $p\text{-}(CH_3OC_6H_4)_3CH(D) + (C_6H_5)_3CBF_4 \longrightarrow p\text{-}(CH_3OC_6H_4)_3CBF_4 + (C_6H_5)_3CH(D)$

spectra 1-12

For the title reaction the amount of reactants used for each run ranged between 0.267×10^{-3} and 0.368×10^{-3} moles (0.0894 and 0.1229 g). In each case, the reactants were dissolved in 4 ml CD_3CN. In some experiments 2 ml CD_3CN and two times the above amount of reactants were used. The reactions were performed in the dry box.

Reaction of Tritolylmethane with Triphenylmethyl Tetrafluoroborate (spectra 13-14):

(2) $p\text{-}(CH_3C_6H_4)_3CH(D) + (C_6H_5)_3CBF_4 \longrightarrow p\text{-}(CH_3C_6H_4)_3CBF_4 + (C_6H_5)_3CH(D)$

spectra 13-14

For the reaction of tritolylmethane with the triphenylmethyl tetrafluoroborate maximum concentrations of reactants were used amounting to about 0.6×10^{-3} moles (0.18 g) in 1 ml CD_3CN. The reactions were performed in the dry box.

Reaction of Trianisylmethane with Anisyldiphenylmethyl Tetrafluoroborate (spectra 15-20):

(3) $p\text{-}(CH_3OC_6H_4)_3CH(D) + p\text{-}(CH_3OC_6H_4)(C_6H_5)_2CBF_4 \longrightarrow p\text{-}(CH_3OC_6H_4)_3CBF_4$
$+ p\text{-}(CH_3OC_6H_4)(C_6H_5)_2CH(D)$ spectra 15-20

The reaction of trianisylmethane with anisyldiphenylmethyl tetrafluoroborate was carried out in the same way as the above reaction in terms of quantities and conditions.

Reaction of Triphenylmethane with Triphenylmethyl Tetrafluoroborate (spectra 21-24):

(4) $(C_6H_5)_3{}^{13}CH + (C_6H_5)_3CBF_4 \longrightarrow (C_6H_5)_3{}^{13}CBF_4 + (C_6H_5)_3CH$

spectra 21-24

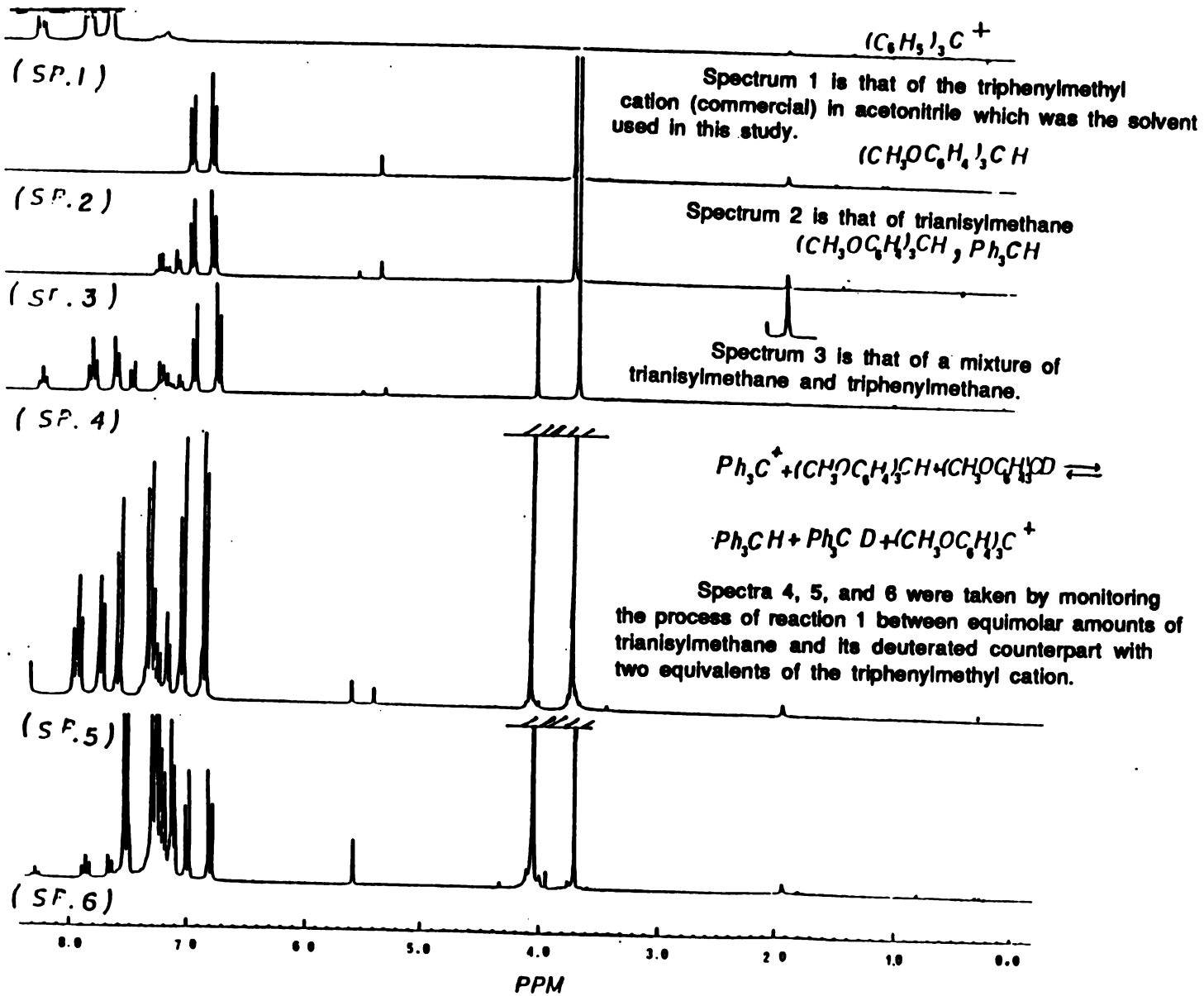
For the title reaction 0.210 g of triphenylmethyl tetrafluoroborate and 0.164 g of triphenylmethane having the central carbon labeled at the methine carbon with 50% C-13 were reacted in 2 ml CD_3CN.

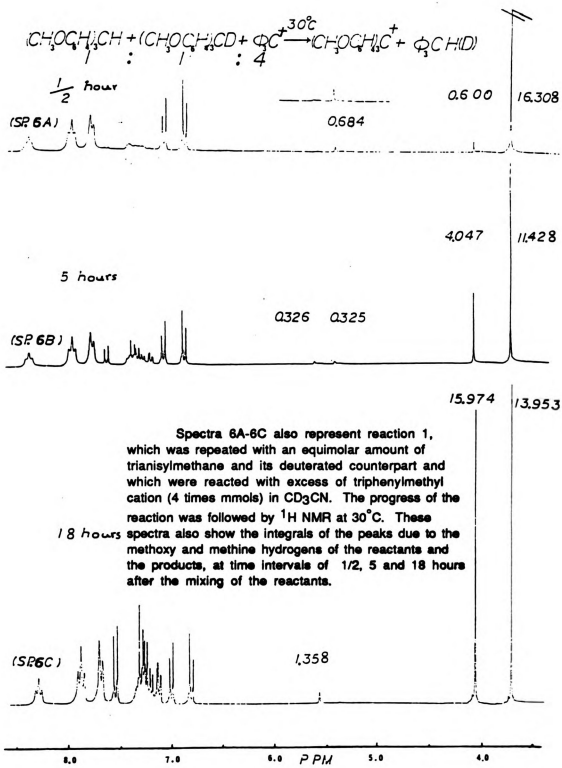
A Bruker 250 MHz NMR instrument was used to study all these reactions. In a typical reaction, the reactants, in 1 : 1 ratio were weighed in two separate vials. Acetonitrile-d_3, 1 or 2 ml, was added to the first vial containing the carbocation and the solution was transferred to the second vial which contained the hydrocarbon. Zero time was assigned at the onset of the mixing. After the solution was transferred into an NMR tube, the sample was placed in the probe that was kept at constant temperature and spectral measurements were taken.

The Relaxation Delay value for the ^1H NMR program which was used in this study was optimized to twenty for the reaction of trianisylmethane and triphenylmethyl tetrafluoroborate, at a time when the rate of product formation was practically zero.

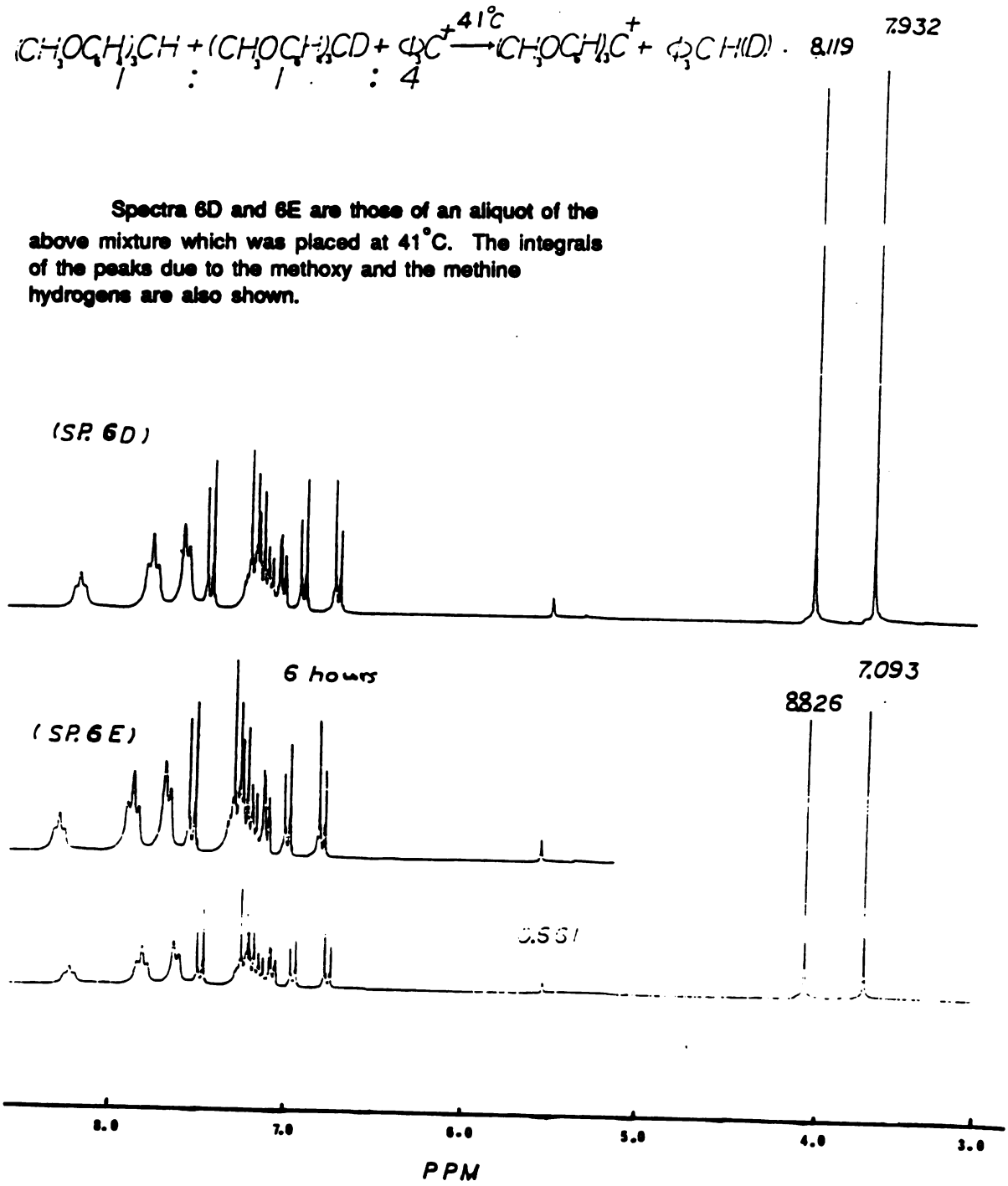
Each experiment was performed twice with freshly prepared starting materials. In the second run the acetonitrile was added first to the hydrocarbon and then transferred to the vial containing the carbocation.

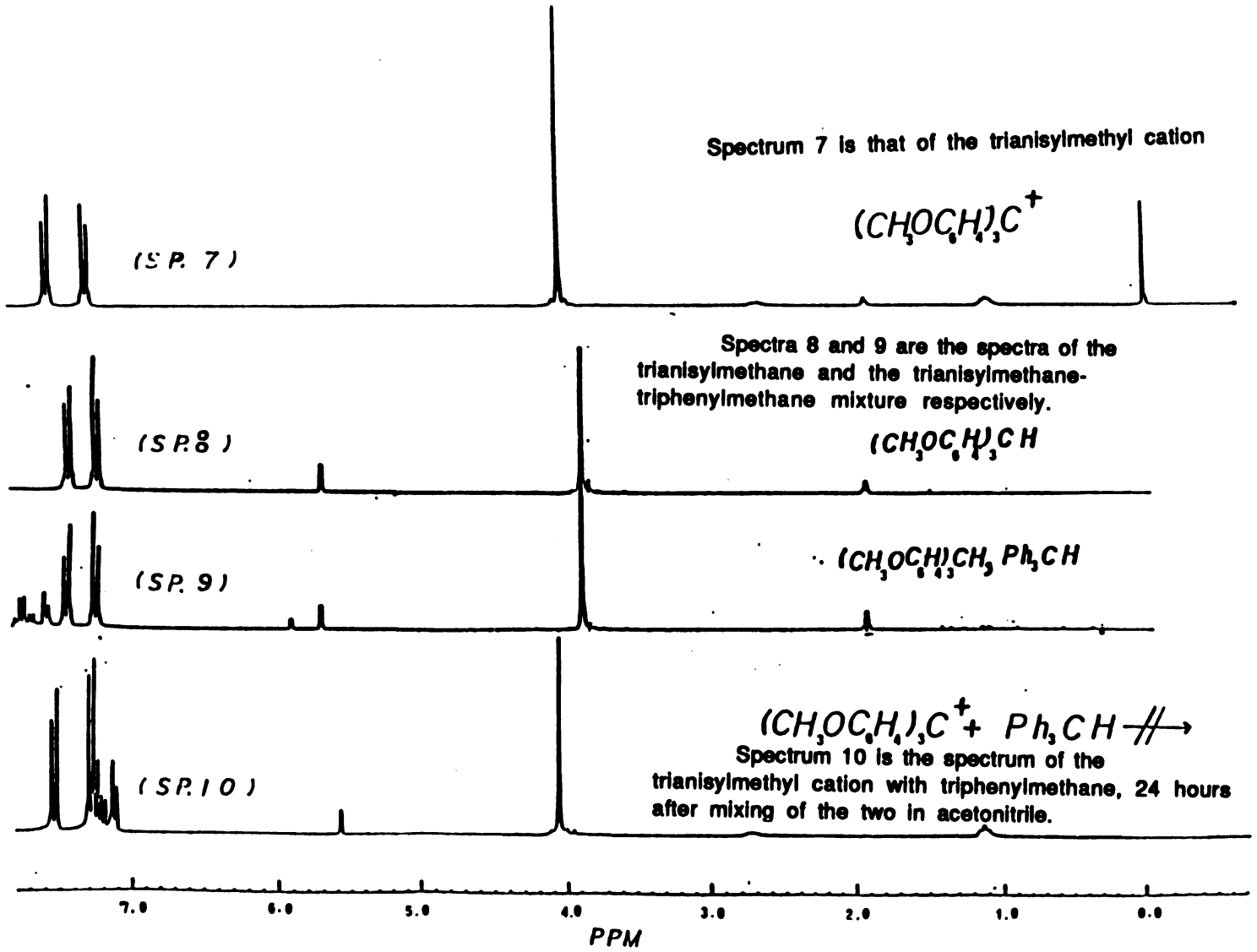
The following spectra, 1-24, are representative of the reactions studied:


$(C_6H_5)_3C^+$
(SP.1)
Spectrum 1 is that of the triphenylmethyl cation (commercial) in acetonitrile which was the solvent used in this study.
$(CH_3OC_6H_4)_3CH$
(SP.2)
Spectrum 2 is that of trianisylmethane
$(CH_3OC_6H_4)_3CH$, Ph_3CH
(SP.3)
Spectrum 3 is that of a mixture of trianisylmethane and triphenylmethane.
(SP.4)
$Ph_3C^+ + (CH_3OC_6H_4)_3CH + (CH_3OC_6H_4)_3CD \rightleftharpoons$
$Ph_3CH + Ph_3CD + (CH_3OC_6H_4)_3C^+$
Spectra 4, 5, and 6 were taken by monitoring the process of reaction 1 between equimolar amounts of trianisylmethane and its deuterated counterpart with two equivalents of the triphenylmethyl cation.
(SP.5)
(SP.6)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM



Spectra 6A-6C also represent reaction 1, which was repeated with an equimolar amount of trianisylmethane and its deuterated counterpart and which were reacted with excess of triphenylmethyl cation (4 times mmols) in CD_3CN. The progress of the reaction was followed by ^1H NMR at 30°C. These spectra also show the integrals of the peaks due to the methoxy and methine hydrogens of the reactants and the products, at time intervals of 1/2, 5 and 18 hours after the mixing of the reactants.


41°C
8.119
7.932
Spectra 6D and 6E are those of an aliquot of the above mixture which was placed at 41°C. The integrals of the peaks due to the methoxy and the methine hydrogens are also shown.
(SP. 6D)
6 hours
7.093
8.826
(SP. 6E)
3.581
8.0
7.0
6.0
5.0
4.0
3.0
PPM



Spectrum 7 is that of the trianisylmethyl cation

$(CH_3OC_6H_4)_3C^+$

Spectra 8 and 9 are the spectra of the trianisylmethane and the trianisylmethane-triphenylmethane mixture respectively.

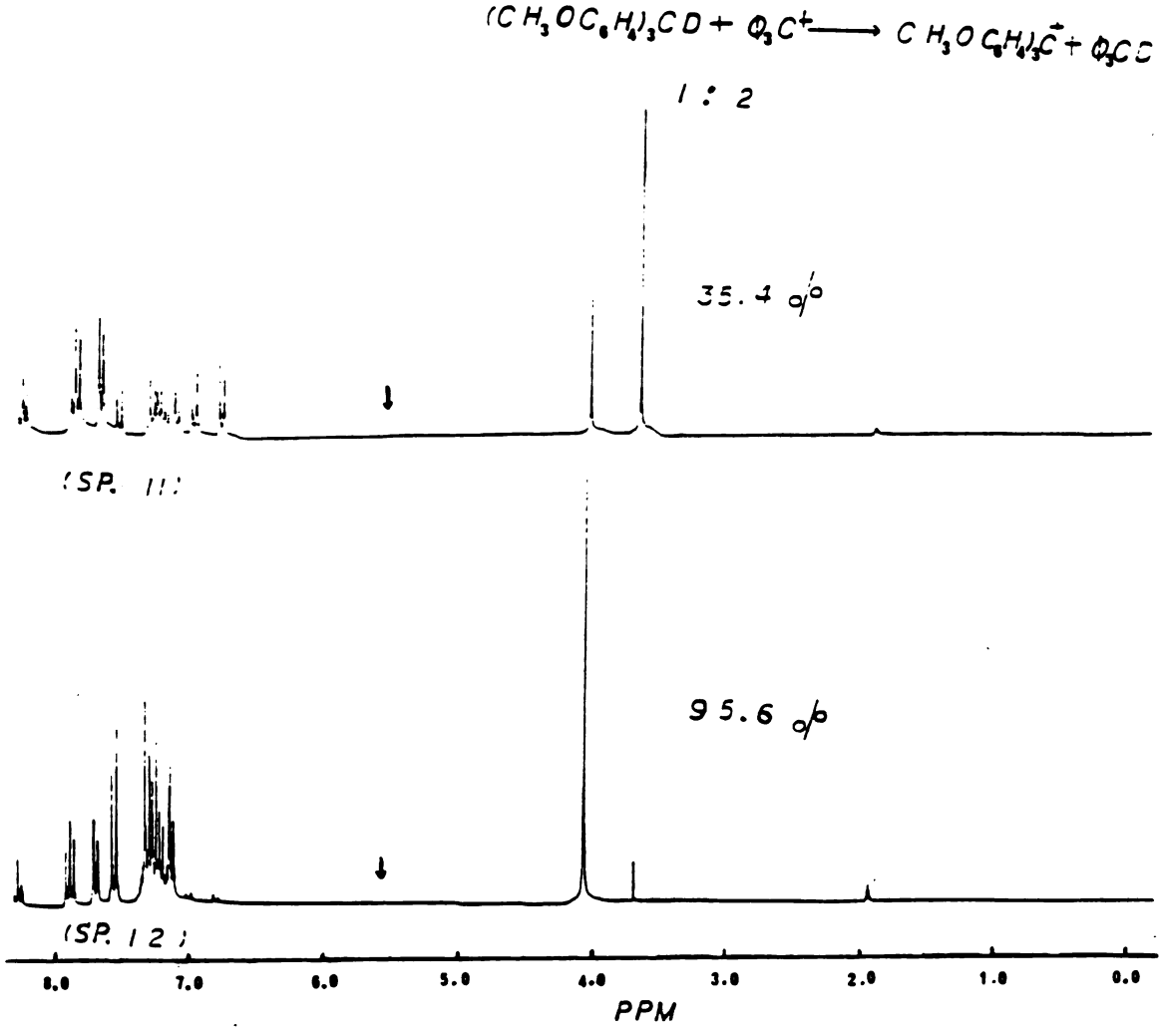
$(CH_3OC_6H_4)_3CH$

$(CH_3OC_6H_4)_3CH$, Ph_3CH

$(CH_3OC_6H_4)_3C^+ + Ph_3CH \not\rightarrow$

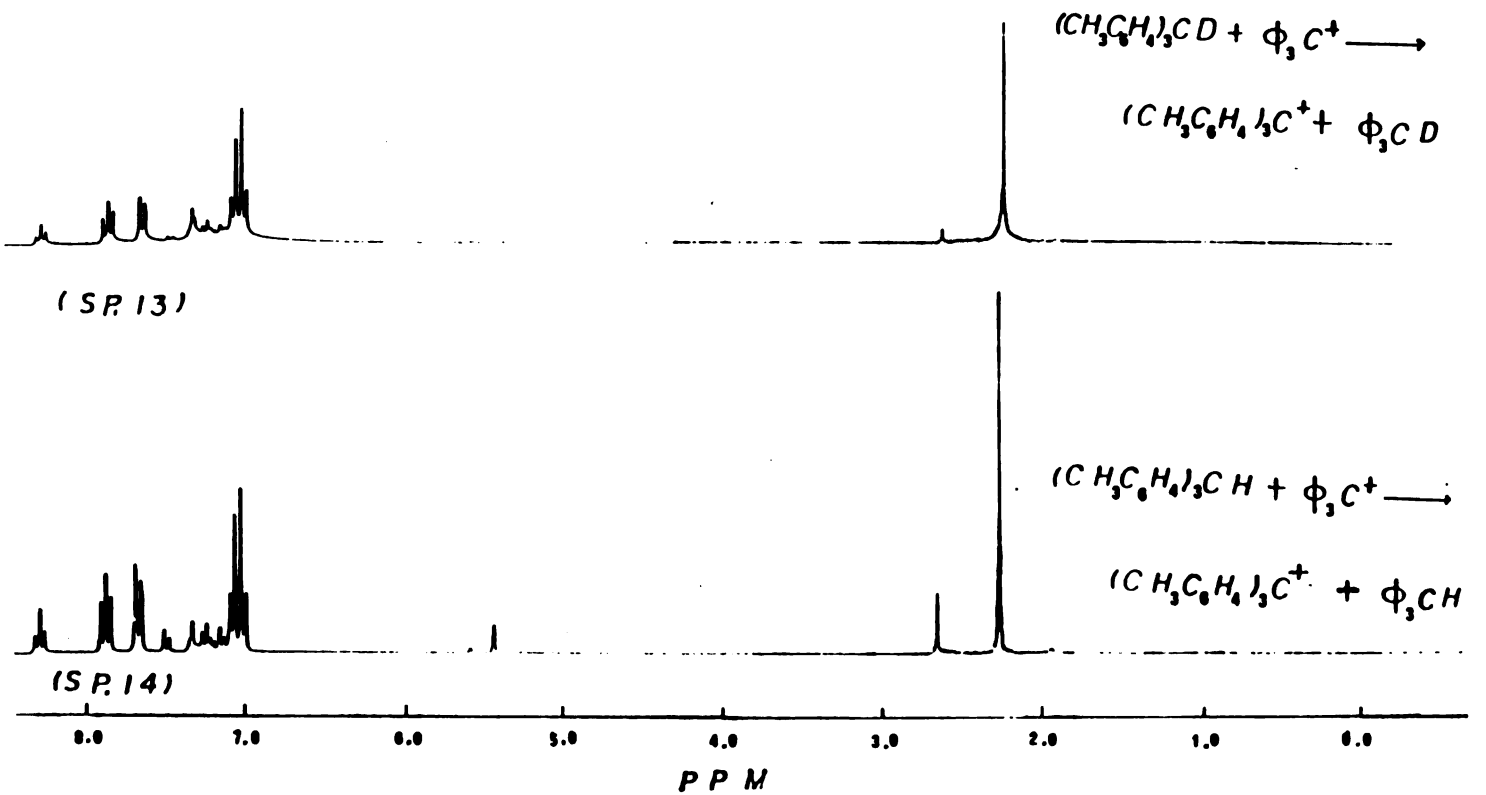
Spectrum 10 is the spectrum of the trianisylmethyl cation with triphenylmethane, 24 hours after mixing of the two in acetonitrile.

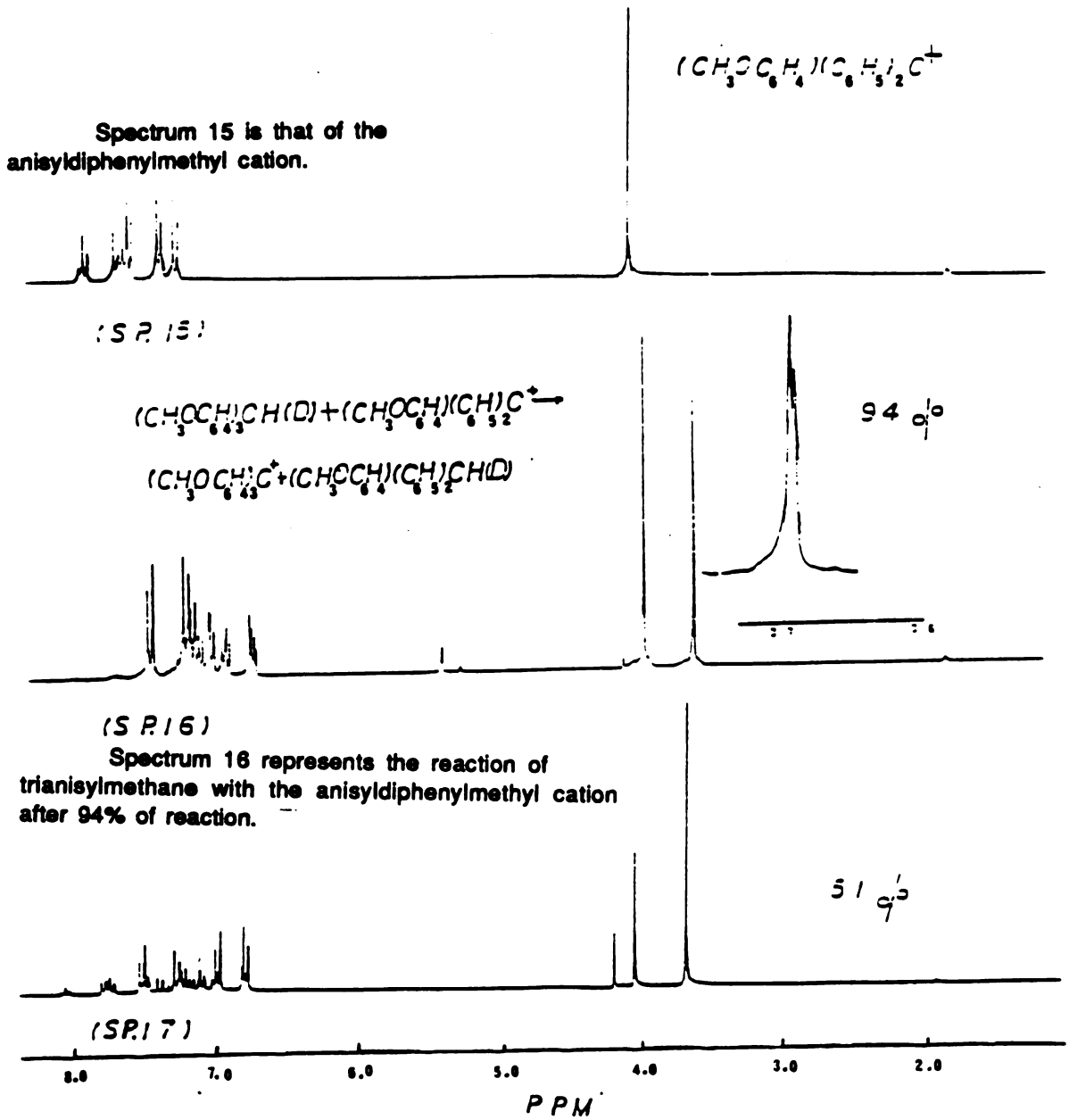
Spectra 11 and 12 represent the reaction of deuterated trianisylmethane with twice as many moles of the triphenylmethyl cation, after 35.4% and 95.6% of the hydrocarbon was reacted. These spectra show no peaks in the area between 5 ppm and 6 ppm.



Spectrum 13 represents the reaction (2) between deuterated tritolylmethane and the triphenylmethyl cation.

Spectrum 14 represents the reaction of tritoluomethane with the triphenylmethyl cation.

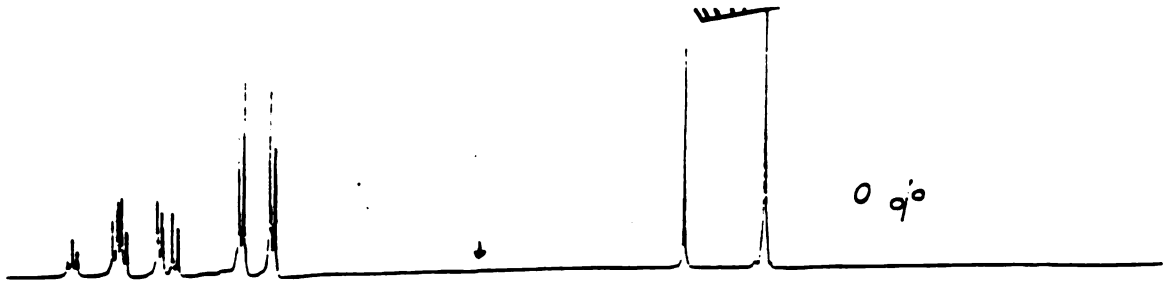




Spectrum 15 is that of the anisyldiphenylmethyl cation.

Spectrum 16 represents the reaction of trianisylmethane with the anisyldiphenylmethyl cation after 94% of reaction.

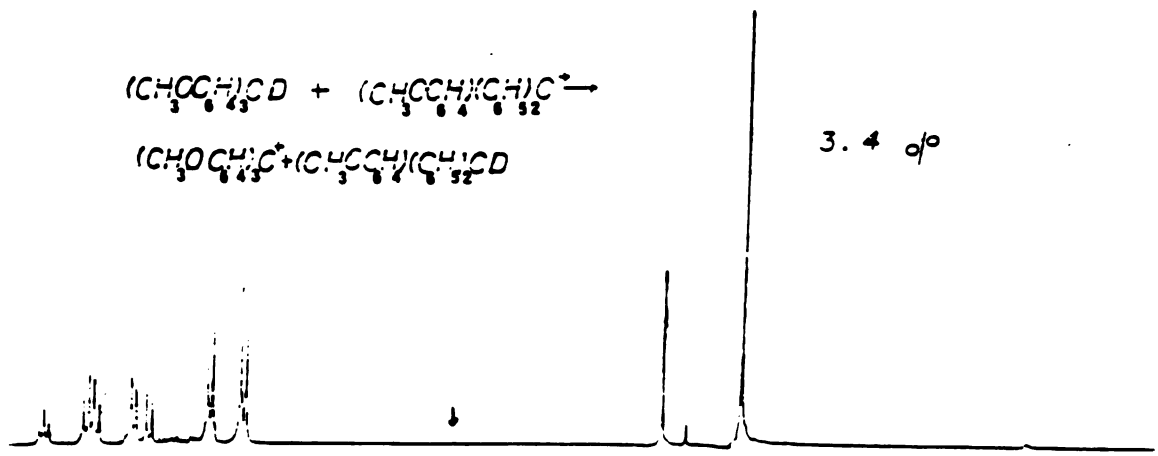
Spectrum 17 is a representative spectrum for reaction of the anisyldiphenylmethyl cation with deuterated trianisylmethane after 51% reaction completion. The peaks shown in spectrum 16 also appear in this spectrum, except for the peaks due to the methine hydrogens; no peaks are detected at 5.49 ppm or 5.36 ppm.



(SP 18)

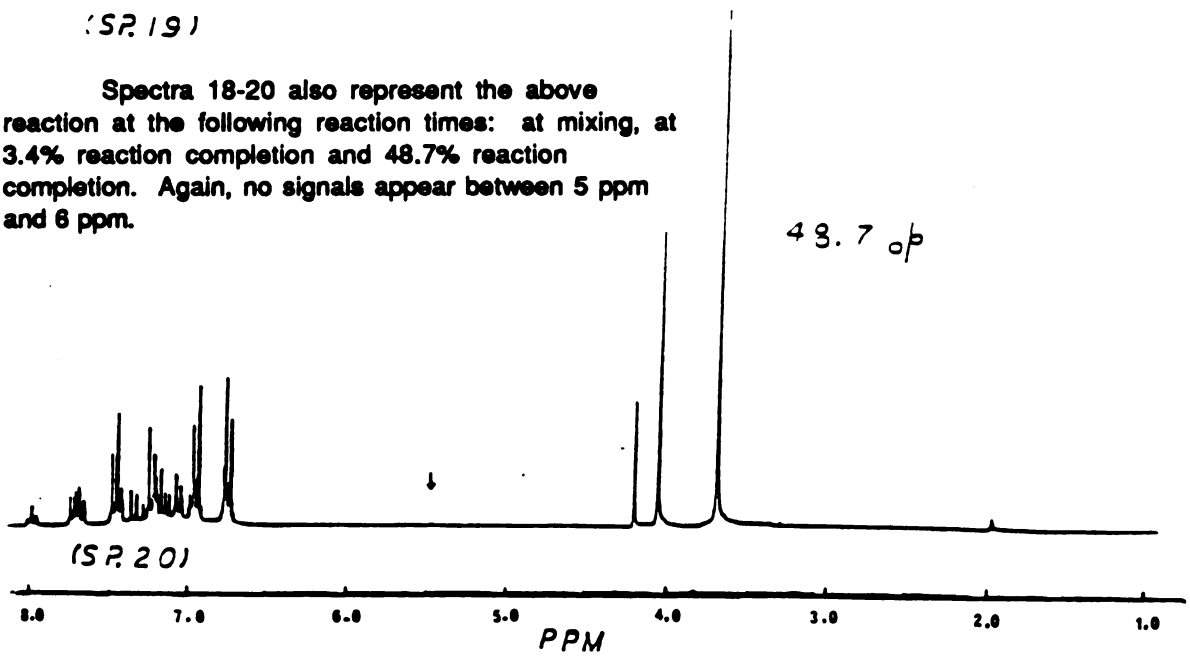
$(CH_3OC_6H_4)_3CD + (CH_3CC_6H_4)(C_6H_5)_2C^+ \rightarrow$

$(CH_3OC_6H_4)_3C^+ + (CH_3CC_6H_4)(C_6H_5)_2CD$



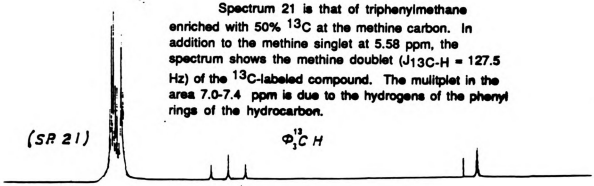
(SP 19)

Spectra 18-20 also represent the above reaction at the following reaction times: at mixing, at 3.4% reaction completion and 48.7% reaction completion. Again, no signals appear between 5 ppm and 6 ppm.

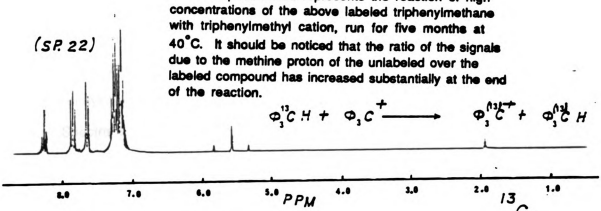


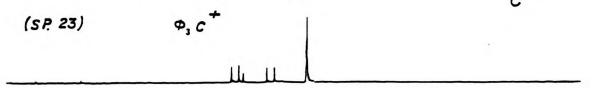
(SP 20)

Spectrum 21 is that of triphenylmethane enriched with 50% ^{13}C at the methine carbon. In addition to the methine singlet at 5.58 ppm, the spectrum shows the methine doublet (J_{13C-H} = 127.5 Hz) of the ^{13}C-labeled compound. The mulitplet in the area 7.0-7.4 ppm is due to the hydrogens of the phenyl rings of the hydrocarbon.

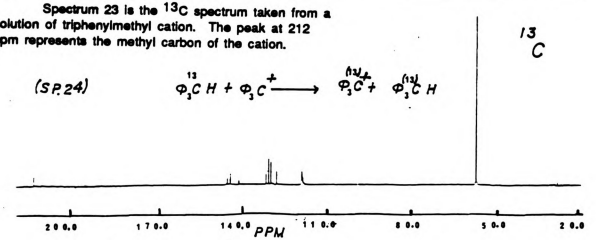


Spectrum 22 represents the reaction of high concentrations of the above labeled triphenylmethane with triphenylmethyl cation, run for five months at 40°C. It should be noticed that the ratio of the signals due to the methine proton of the unlabeled over the labeled compound has increased substantially at the end of the reaction.





Spectrum 23 is the ^{13}C spectrum taken from a solution of triphenylmethyl cation. The peak at 212 ppm represents the methyl carbon of the cation.



Spectrum 24 which is a ^{13}C spectrum, was taken from the same sample the same day the spectrum 22 was taken. It should be noticed that the ratio of the signal due to the methyl carbon over the other signals in spectrum 23 is larger compared to that of spectrum 22.

Spectrum 1 is that of the triphenylmethyl cation (commercial) in acetonitrile. The small pentet peak at 1.93 ppm belongs to the acetonitrile (D, 99.6%) which was the solvent used for this study. The multiple peaks shown downfield between, 7.7-8.3 ppm, belong to the hydrogens of the phenyl rings of the cation.

Spectrum 2 is that of trianisylmethane and shows singlet peaks at 3.68 ppm and 5.37 ppm representing the methoxy groups and the methine hydrogen respectively as well as two doublets at 7.8 ppm and 8.1 ppm representing the hydrogens of the phenyl rings.

Spectrum 3 is that of a mixture of trianisylmethane and triphenylmethane. In this spectrum, in addition to the peaks shown in spectrum 2, are shown a singlet peak due to the methine hydrogen of the triphenylmethane (5.55 ppm) and multiple peaks due to the phenyl hydrogens of the triphenylmethane (8.1-8.4 ppm).

Spectra 4, 5, and 6 were taken by monitoring the process of reaction 1 between equimolar amounts of trianisylmethane and its deuterated counterpart with two equivalents of the triphenylmethyl cation. In spectra 4 and 5 in addition to the peaks of the triphenylmethyl cation, trianisylmethane and triphenylmethane, appear the peaks due to the trianisylmethyl cation. These are a singlet at 4.05 ppm from the methoxy groups and two doublets at 8.3 ppm and 8.6 ppm representing the hydrogens of the phenyl rings. In spectrum 6 the peak at 5.37 ppm, which was due to the trianisylmethane methine hydrogen, has disappeared.

Spectra 6A-6C also represent reaction 1, which was repeated with an equimolar amount of trianisylmethane and its deuterated counterpart and which were reacted with excess of triphenylmethyl cation (4 times mmols) in CD_3CN. The progress of the reaction was followed by ^1H NMR at 30°C. These spectra also show the integrals of the peaks due to the methoxy and methine hydrogens of the reactants and the products, at time intervals of 1/2, 5 and 18 hours after the mixing of the reactants.

Spectra 6D and 6E are those of an aliquot of the above mixture which was placed at 41°C. The integrals of the peaks due to the methoxy and the methine hydrogens are also shown.

Spectrum 7 is that of the trianisylmethyl cation and shows a singlet due to the methoxy group at 4.05 ppm and two doublets due to the hydrogens of the phenyl rings at 7.3 ppm and 7.5 ppm.

Spectra 8 and 9 are the spectra of the trianisylmethane and the trianisylmethane-triphenylmethane mixture respectively.

Spectrum 10 is the spectrum of the trianisylmethyl cation with triphenylmethane, 24 hours after mixing of the two in acetonitrile.

Spectra 11 and 12 represent the reaction of deuterated trianisylmethane with twice as many moles of the triphenylmethyl cation, after 35.4% and 95.6% of the hydrocarbon was reacted. These spectra show no peaks in the area between 5 ppm and 6 ppm.

Spectrum 13 represents the reaction (2) between deuterated tritolylmethane and the triphenylmethyl cation. In this spectrum, the signal due to the methyl groups of the reactant is a singlet at 2.22 ppm and that due to the methyls of the product is a singlet at 2.61 ppm. The AA'BB' signal of the hydrogens of the phenyl rings of the tritolylmethane appears in the area 6.9-7.1 ppm.

Spectrum 14 represents the reaction of tritolylmethane with the triphenylmethyl cation. The methine hydrogen of the reactant appears as a singlet at 5.40 ppm and that of the product at 5.55 ppm.

Spectrum 15 is that of the anisyldiphenylmethyl cation. The methoxy group of the cation is a singlet at 4.19 ppm and the hydrogens of the phenyl rings appear as a multiplet in the area between 7.1 ppm and 7.9 ppm.

Spectrum 16 represents the reaction of trianisylmethane with the anisyldiphenylmethyl cation after 94% of reaction. The methine hydrogen of the product

hydrocarbon appears as a singlet at 5.49 ppm and that of the reactant hydrocarbon at 5.36 ppm. Four singlets representing the methoxy groups of the reactants and the products appear in the area between 3.5 ppm and 4.5 ppm. The signal at 4.19 ppm is that of the methoxy group of the anisyldiphenylmethyl cation; that at 4.05 ppm is the signal of the methoxy groups of the trianisylmethyl cation; and those at 3.69 ppm (3.692 and 3.695) are the signals due to the methoxy groups of the two hydrocarbons.

Spectrum 17 is a representative spectrum for reaction of the anisyldiphenylmethyl cation with deuterated trianisylmethane after 51% reaction completion. The peaks shown in spectrum 16 also appear in this spectrum, except for the peaks due to the methine hydrogens; no peaks are detected at 5.49 ppm or 5.36 ppm.

Spectra 18-20 also represent the above reaction at the following reaction times: at mixing, at 3.4% reaction completion and 48.7% reaction completion. Again, no signals appear between 5 ppm and 6 ppm.

Spectrum 21 is that of triphenylmethane enriched with 50% ^{13}C at the methine carbon. In addition to the methine singlet at 5.58 ppm, the spectrum shows the methine doublet ($J_{^{13}C\text{-}H}$ = 127.5 Hz) of the ^{13}C-labeled compound. The mulitplet in the area 7.0-7.4 ppm is due to the hydrogens of the phenyl rings of the hydrocarbon.

Spectrum 22 represents the reaction of high concentrations of the above labeled triphenylmethane with triphenylmethyl cation, run for five months at 40°C. It should be noticed that the ratio of the signals due to the methine proton of the unlabeled over the labeled compound has increased substantially at the end of the reaction.

Spectrum 23 is the ^{13}C spectrum taken from a solution of triphenylmethyl cation. The peak at 212 ppm represents the methyl carbon of the cation.

Spectrum 24 which is a ^{13}C spectrum, was taken from the same sample the same day the spectrum 22 was taken. It should be noticed that the ratio of the signal due to the methyl carbon over the other signals in spectrum 23 is larger compared to that of spectrum 22.

RESULTS AND DISCUSSION

Calculations of rate constants and kinetic isotope effects ($^{k}H/^{k}D$):

The rate constants and kinetic isotope effects of reactions (1), (2), and (3) were determined at several different temperatures.

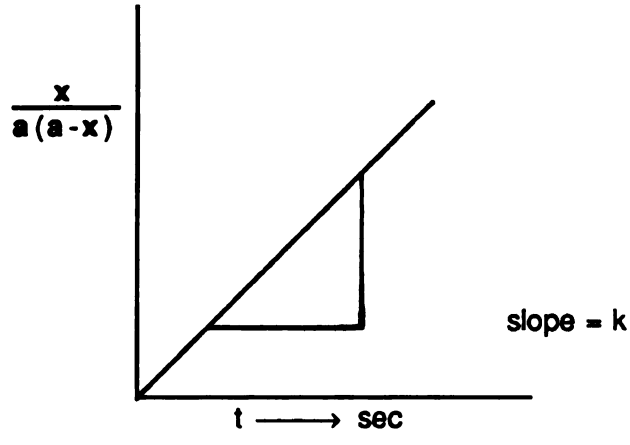
All the reactions were second order, 1:1, and were followed by NMR.

For the second order reaction

$$A + B \longrightarrow C + B$$

the rate constants were calculated from the equation:

$$k = \frac{x}{a(a-x)} \cdot \frac{1}{t}$$



where x is the product's concentration at time t and a is the initial concentration of the starting materials.

Reaction of Trianisylmethane with Triphenylmethyl Tetrafluoroborate (1):

Reaction (1) was carried out at three different temperatures; namely 22°, 30°, 40°C. From each sample run at a given temperature (22°, 30°, 40°C), an aliquot was taken and run at 26°C, to show the consistency of the measurements. The amount of reactants used for each run ranged between 0.000267 and 0.000368 moles (0.0894

and 0.1229 grams). In each case the reactants were dissolved in 1 ml acetonitrile-d_3. In some experiments 2 ml solvent and two times the above amounts of reactants were used. Each NMR tube containing the sample was placed in the NMR probe at constant temperature and measurements were taken up until 15-20% reaction completion, which usually took 3-4 hours, for the hydrogen compounds. The reaction of the deuterated trianisylmethane proceeded much more slowly. Consequently, the concentration of the deuterated reactants was approximately 2-3 times larger than that of the undeuterated ones. This higher concentration required 8-9 hours for 10% reaction completion.

Rate constants were calculated from the integrated areas of the methoxy groups of the products and the reactants. The sum of the area under the peak of the methoxy group at 3.69 ppm (reactant) plus the area under the methoxy peak at 4.05 ppm (product), denoted as A_4 and A_3 respectively, equal the initial number of moles of trianisylmethane a.

$$\text{So} \qquad A_3W + A_4W = a$$

$$W = \frac{a}{A_3 + A_4}$$

$$X = A_3W$$

For solution volume* V:

$$x = \frac{1000x}{v}$$

$$a = \frac{1000a}{v}$$

and the rate constant in time t can be written as

$$k = \frac{A_3v}{1000aA_4} \cdot \frac{1}{t}$$

---

* The volume of the solutions was measured as follows: The same amount of reagents for each individual run was placed in a 1 ml or 2 ml volumetric flask. Either 1 ml or 2 ml of solvent was added to the flask. The volume of the solution above the line which indicates the 1 ml or 2 ml was measured with a 0.5 ml syringe.

The k is the slope of $\frac{A_3 v}{1000 a A_4}$ versus t. Using the least squares method the slope, the intercept, the slope deviation (standard) and the 95 percentage confidence slope interval, for each run in each temperature were calculated. The computerized data and results appear in the appendix (page 96-107, 138) as well as the computer program (pages 94-95) which was used for the calculations. Also in the appendix appear the computerized $^kH/^kD$ (page 138). The ± deviation of this interval was calculated according to the equation:

$$\pm(\Delta b)^2 = (\frac{1}{k_D})^2(\Delta^k H)^2 + [(\frac{1}{k_D{}^2})^k H]^2 \Delta^k D^2$$

(Δb = deviation of the $\frac{k_H}{k_D}$, $\Delta^k H$ = slope deviation of the ^kH; $\Delta^k D$ = slope deviation of the ^kD). The results from these calculations are summarized in Table 1 and Table 4. Tables 2 and 3 summarize the rate constants for the reactions carried out at 26°C.

Reaction of Tritolylmethane with Triphenylmethyl Tetrafluoroborate (2):

The reaction of tritolylmethane with triphenylmethyl tetrafluoroborate is extremely slow. Consequently, maximum concentrations of reactants were used amounting to about 0.0006 moles (0.18 grams) in 1 ml CD_3CN. The protiated compounds were measured up to 10-15% reaction completion, which required 4-10 days, and the deuterated counterparts until 3-6% reaction completion, which required 10-15 days. An oven was used for the 30°C measurements and a sund bath for 25.5°C and 39.5°C. The reactions with hydrogen and deuterium reactants were done simultaneously and were at the same temperature in close proximity.

For reaction (2), the areas of the methyl group peaks of reactant and product, A_4 and A_3 respectively, were used. Calculations of the slope (rate constant), the intercept, the slope deviation (standard), the 95 percentage confidence slope interval and the $^kH/^kD$, for each run at each temperature were carried out as above (appendix pages 108-119, 139). Tables 5 and 6 summarize the results from these calculations.

Reaction of Trianisylmethane with Anisyldiphenylmethyl Tetrafluoroborate (3):

Reaction (3) was carried out in the same way as reaction (2) in terms of quantities of compounds and temperature used. The two areas under the methoxy peaks, the one in the reactant carbocation at 4.19 ppm, which represents one methoxy group, and the other in the product carbocation at 4.05 ppm, which represents three methoxy groups, were donated as A_3 and A_4 respectively. So in this case

$$A_3W + \frac{A_4}{3}W = a$$

$$x = \frac{A_4}{3}W$$

and the rate constant for volume v at time t can be written as

$$k = \frac{v \cdot A_4}{3000 \cdot a \cdot A_3} \cdot \frac{1}{t}$$

The computerized data and results for each run in each temperature appear in the appendix (pages 126-137, 140) as well as the computer program which was used for this reaction (pages 124-125). These results are summarized in Tables 7 and 8.

Table 1. Rate constants and isotope effects of the reaction of trianisylmethane with triphenylmethyl tetrafluoroborate.

t °C	k_H^*	k_D^*	k_H/k_D^*	k_H^{**}	k_D^{**}	k_H/k_D^{**}
22.0±0.2	$(4.63\pm0.36)\times10^{-5}$	$(5.72\pm0.20)\times10^{-6}$	8.1±0.7	$(3.90\pm0.26)\times10^{-5}$	$(5.85\pm0.17)\times10^{-6}$	6.6±0.5
30.0±0.2	$(6.39\pm0.57)\times10^{-5}$	$(8.62\pm0.30)\times10^{-6}$	7.4±0.7	$(8.07\pm0.13)\times10^{-5}$	$(1.11\pm0.03)\times10^{-5}$	7.3±0.2
40.0±0.2	$(1.69\pm0.05)\times10^{-4}$	$(2.41\pm0.07)\times10^{-5}$	7.0±0.3	$(1.51\pm0.08)\times10^{-4}$	$(2.12\pm0.02)\times10^{-5}$	7.1±0.4

k_H, k_D in units of $M^{-1}S^{-1}$

* = first run
** = second run

Tables 2. Rate constants (^{k}H) from aliquot solutions taken from the different runs of the reaction of trianisylmethane with triphenylmethyl tetrafluoroborate and stablized at 26°C.

From solution for the run at °C	Temperature °C	a_{moles}	v cm^3	t sec	A_3	A_4	^{k}H $M^{-1}sec^{-1}$
22.0±0.2	26.0±0.0	0.000249	1.130	14376	1.842	11.805	$4.92x10^{-5}$
				14946	1.879	11.240	$5.07x10^{-5}$
30.0±0.2	26.0±0.1	0.000283	1.145	14496	3.271	16.190	$5.64x10^{-5}$
				15156	1.702	8.025	$5.66x10^{-5}$
40.0±0.2	26.0±0.1	0.000173	1.080	11376	1.018	10.845	$5.15x10^{-5}$
				12156	2.187	22.452	$5.00x10^{-5}$
				13029	1.201	11.292	$5.10x10^{-5}$

Table 3. Rate constants (^{k}D) from aliquot solutions taken from the different runs of the reaction of trianisylmethane-1-d with triphenylmethyl tetrafluoroborate and stabilized at 26°C.

From solution for the run at °C	Temperature °C	a_{moles}	v cm^3	t sec	A_3	A_4	^{k}D $M^{-1}sec^{-1}$
22.0±0.2	26.0±0.7	0.000603	1.270	36516	1.965	20.865	$5.42x10^{-6}$
				37056	2.146	20.966	$5.80x10^{-6}$
30.0±0.2	26.0±0.5	0.000527	1.240	26556	1.136	17.716	$5.69x10^{-6}$
				27156	1.153	16.995	$5.89x10^{-6}$
				27876	1.149	17.697	$5.49x10^{-6}$
				28476	1.199	16.598	$5.97x10^{-6}$
40.0±0.2	26.0±0.2	0.000485	1.255	25656	0.758	12.117	$6.31x10^{-6}$
				27816	0.835	11.926	$6.51x10^{-6}$
				29676	0.837	11.831	$6.17x10^{-6}$
				30876	0.928	11.658	$6.67x10^{-6}$

Table 4. Isotope effects for the reaction of trianisylmethane with triphenylmethyl tetrafluoroborate.

t °C	k_H/k_D*	k_H/k_D**
22.0±0.2	8.1±0.7	6.6±0.5
30.0±0.2	7.4±0.7	7.3±0.2
40.0±0.2	7.0±0.3	7.1±0.4

* = first run
** = second run

Table 5. Rate constants and isotope effects of the reaction of tritolylmethane with triphenylmethyl tetrafluoroborate.

t °C	k_H^*	k_D^*	k_H/k_D^*	k_H^{**}	k_D^{**}	k_H/k_D^{**}
25.0±0.2	$(2.83\pm0.17)\times10^{-7}$	$(4.35\pm1.6)\times10^{-8}$	6.5±2.4	$(3.15\pm0.15)\times10^{-7}$	$(4.48\pm0.27)\times10^{-8}$	7.0±0.5
30.0±0.2	$(5.67\pm0.14)\times10^{-7}$	$(6.75\pm0.56)\times10^{-8}$	8.4±0.7	$(5.31\pm0.16)\times10^{-7}$	$(6.03\pm1.00)\times10^{-8}$	8.8±1.5
40.0±0.2	$(1.57\pm0.06)\times10^{-6}$	$(1.78\pm0.08)\times10^{-7}$	8.8±0.5	$(1.42\pm0.04)\times10^{-6}$	$(1.49\pm0.07)\times10^{-7}$	9.5±0.5

k_H, k_D in units of $M^{-1}S^{-1}$

* = first run
** = second run

Table 6. The isotope effects for the reaction of tritolylmethane with triphenylmethyl tetrafluoroborate.

t °C	k_H/k_D*	k_H/k_D**
25.0±0.2	6.5±2.4	7.0±0.5
30.0±0.2	8.4±0.7	8.8±1.5
40.0±0.2	8.8±0.5	9.5±0.5

* = first run
** = second run

Table 7. Rate constants and isotope effects of the reaction of trianisylmethane with the anisyldiphenylmethyl tetrafluoroborate.

t °C	k_H^*	k_D^*	k_H/k_D^*	k_H^{**}	k_D^{**}	k_H/k_D^{**}
26.0±0.2	$(5.02\pm0.14)\times10^{-7}$	$(5.85\pm0.76)\times10^{-8}$	8.6±1.1	$(4.51\pm0.02)\times10^{-7}$	$(4.37\pm0.30)\times10^{-8}$	10.3±0.7
30.0±0.2	$(9.09\pm0.19)\times10^{-7}$	$(1.00\pm0.06)\times10^{-7}$	9.1±0.6	$(8.99\pm0.32)\times10^{-7}$	$(7.05\pm0.49)\times10^{-8}$	12.7±1.0
40.0±0.2	$(2.51\pm0.07)\times10^{-6}$	$(2.82\pm0.06)\times10^{-7}$	8.9±0.3	$(2.47\pm0.03)\times10^{-6}$	$(2.75\pm0.05)\times10^{-7}$	9.0±0.2

k_H, k_D in units of $M^{-1}S^{-1}$

* = first run
** = second run

Table 8. Isotope effects for the reaction of trianisylmethane with anisyldiphenylmethyl tetrafluoroborate.

t °C	k_H/k_D*	k_H/k_D**
26.0±0.2	8.6±1.1	10.3±0.7
30.0±0.2	9.1±0.6	12.7±1.0
40.0±0.2	8.9±0.3	9.0±0.2

* = first run
** = second run

Investigation of the magnitude of the isotope effect for the reaction of the trianisylmethane with the triphenylmethyl tetrafluoroborate (1):

The large value of the isotope effect for reaction (1) was also confirmed by the results of the following experiment: An equimolar amount of trianisylmethane and its deuterated counterpart (0.147 mmol) was reacted with triphenylmethyl tetrafluoroborate (4x0.147 mmol), in acetonitrile (1 ml), and the progress of the reaction was followed by ^1H NMR. Two reactions were run at 30°C and 41°C, spectra 6A-6E. At 30°C and at t=5 hrs, half of the hydride was transfered; however, the methoxy peak of the product was quite small compared with that of the starting material. This indicates that only a small amount of deuterium was transferred (sp. 6B). At t=18 hrs, sp. 6C, whereas hydride transfer was nearly complete, the methoxy peaks showed the presence of a large quantity of unreacted deuterated starting material. Likewise, at 41°C and at t=6 hrs, whereas hydride transfer was almost complete, again the methoxy peaks indicated that only a small fraction of deuterated starting material was reacted (sp. 6E). The spectra 6A-6E and the integration data shown confirm the large magnitude of the kinetic isotope effect.

Search for possible hydride attack on carbons other[4d] than C-1 of the cations:

The possiblility of hydride attacking the phenyl rings of the triphenylmethyl tetrafluoroborate followed by hydride rearrangments to the methine carbon was investigated as follows:

Trianisylmethane-1-d (0.1263 g)and triphenylmethyl tetrafluoroborate (0.2489 g), in about 2 ml CD_3CN, were allowed to react at 40°C until 95% completion. NMR showed no signal at 5.55 ppm where the methine of triphenylmethane absorbs (sp. 12). On high magnification a very small proton peak is detectable which can not be integrated because of its small magnitude. This very small peak is evident as early as when the reaction is only 1-2% complete and its intensity does not change after 95% reaction completion. It is also observed in all the reactions where deuterated compounds

were used. It is probably due: a) to the hydrogen species showing a very weak peak at 2.1 ppm in the ^1H NMR spectrum of the CD_3CN, and which disappears when the reaction is carried out in this solvent or b) to unlabeled trianisylmethane present in the deuterated trianisylmethane which was prepared from «99.9%» $LiAlD_4$.

Reaction of deuterated trianisylmethane and anisyldiphenylmethyl tetrafluoroborate was allowed to proceed to 51% completion. Upon mixing the components the ^1H NMR (spectrum 18) shows no signal at 5.55 ppm, which denotes no anisyldiphenylmethane. After 3.4% reaction, (sp. 19), no signal is detected in this region. Even after three months, at which time 48.7% of reaction has occurred, no signal due to a methine is detectible. If hydrogen rearrangement from the phenyl ring to the carbocation center had occurred, a methine proton at 5.55 ppm would have been detected.

Reaction of triphenylmethane with the triphenylmethyl cation:

The reaction of triphenylmethyl tetrafluoroborate (0.210 g) and triphenylmethane (0.164 g) having the central carbon labeled with ^{13}C (50% excess), reaction (4)

$$(C_6H_5)_3{}^{13}CH + (C_6H_5)_3CBF_4 \rightleftharpoons (C_6H_5)_3{}^{13}CBF_4 + (C_6H_5)_3CH \qquad (4)$$

at 40°C and at high concentration (about 2 ml solvent was used) was run for five months. The reaction was monitored by ^1H NMR in the region of 5-6 ppm (5.32, 5.58, 5.83). As shown in spectrum 22, when compared with spectrum 21 of the starting material, reaction (4) has proceeded. Similarly, ^{13}C NMR analysis of the same reaction corroborated this finding by showing an increase in the intensity of the methine carbon of the cation at 212.6 ppm (compare spectra 23 and 24).

Conclusions

All the reactions studied in this section represent one-step hydride transfer reactions. The transfer occurs from the donor to the acceptor molecule with no new carbon-carbon bonds or any other products having formed.

Investigations of the triphenylmethyl and anisyldiphenylmethyl cation reactions confirm that the only cationic reacting center in the triarylmethyl cations under the conditions of this study is the central carbon. The possibility of hydride attack on the aryl rings of the triarylmethyl cations followed by rearrangement to the methine carbon does not occur to a detectable extent.

The reaction of triphenylmethyl tetraflouroborate and triphenylmethane proceeds very slowly.

The very large isotope effects exhibited by these reactions, slightly larger than the maximum kinetic isotope effect O'Ferral reports for linearity, support a linear transition state for the reaction of triarylmethyl cations with triarylmethanes. The data are not accurate enough to determine activation energy parameters and assess the extent of any quantum mechanical tunnelling.

CHAPTER III

XANTHENE REACTIONS

EXPERIMENTAL

I. Preparations

9-Deuteroxanthene and 9,9-Dideuteroxanthene:

A 30 ml THF solution of 9-xanthone (4 g commercial) was reduced to the corresponding alcohol in a 100 ml round-bottomed flask by gradual and careful addition of excess of $LiAlD_4$ (about 0.5 g) while stirring overnight at room temperature. The excess $LiAlD_4$ was destroyed by water and the THF was evaporated. Ether was added to the flask and the organic layer was separated, was dried over Na_2SO_4, and the solvent was evaporated. The alcohol was then treated like the alcohols in Chapter II with acetyl chloride at room temperature in THF for 40 minutes to yield the chloro derivative. The solvent was then evaporated under vacuum, the chloride redissolved in THF and treated like the chlorides in Chapter II with $LiAlH_4$ or $LiAlD_4$ for 20 minutes at room temperature. The acetonitrile solution of the 9-deuteroxanthene gave spectrum 26 and that of 9,9-dideuteroxanthene spectrum 27.

Xanthyl Cation:

The xanthyl cation (sp. 46) was prepared by the reaction of excess xanthene (0.8 g commercial) with the triphenylmethyl tetrafluoroborate (1.3 g) in CH_3CN (3.5 ml) at room temperature followed by addition of ether (about 4 ml) and cooling that led to the precipitation of xanthyl tetrafluoroborate. The small peak at 3.93 ppm and the impurities shown near the benzene ring protons in the sp. 46 may have originated from the species that exhibited the peak at 2.1 ppm and which disappeared.

2,6-Dimethoxyxanthyl Cation:

The 2,6-dimethoxy-9-xanthone which was used for the preparation of the 2,6-dimethoxyxanthyl cation was prepared according to the procedure described by P. Grover, G. Shah and R. Shah.[16] For this 1 g of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (commercial) was heated with 20 ml of water in a 60 ml volume closed tube at 210°C for 48 hours. The cycloketone formed was crystallized from ethanol. This 2,6-dimethoxy-9-xanthone was reacted with an excess of $LiAlH_4$ in THF to form the corresponding alcohol (m.p. 165-170°C). An excess of this alcohol was then treated with triphenylmethyl tetrafluoroborate in CH_3CN to form the substituted xanthyl cation (sp. 47) under conditions similar to those needed to prepare the xanthyl cation. The 2,6-dimethoxyxanthyl cation was precipitated as the tetrafluoroborate salt by addition of THF, the solid was filtered and washed with THF. This cation reacted with cycloheptatriene in CD_3CN to form the trophylium ion; however, it was unreactive toward triphenylsilane in CD_3CN.

2,6-Dimethoxy-9-Deuteroxanthene:

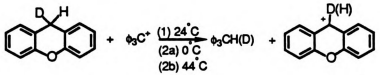
The title compound was prepared by careful addition of an excess of $LiAlD_4$ (about 0.15 g) to a stirred suspension of solid 2,6-dimethoxyxanthyl tetrafluoroborate (1 g) in ether (30 ml) in a 100 ml round-bottomed flask at room temperature. The excess $LiAlD_4$ was destroyed after 20 minutes by water and the organic layer was separated and dried over Na_2SO_4. The white solid deuteroxanthene (m.p. 115-116°C) had an NMR in acetonitrile solution with a characteristic symmetrical triplet due to the C-9 proton at 3.88 ppm (sp. 48).

Dianisylmethyl Perchlorate:

This cation was prepared by a method similar to that used for the formation of anisyldiphenylmethyl tetraflouroborate in Chapter II. When 4,4-dimethoxybenzhydrol (4 g commercial) was treated with perchloric acid (0.022 moles) which was added dropwise to an ice-cooled propionic anhydride solution (70 ml) of the benzhydrol, red crystals of the cation perchlorate formed. The crystals were filtered under argon and washed with petroleum ether (B.P. 35-60°C). The solid cation, whose NMR is shown in spectrum 37, is stable for 1-2 hours at room temperature and for a few days if refrigerated. However, a solution of the cation in CD_3CN decomposed within 30 minutes.

II. Reactions studied

Reaction of 9-Deuteroxanthene with Triphenylmethyl Tetrafluoroborate (spectra 25-36)



(1) & (2) spectra 25-36

The title reaction was carried out by weighing the 9-deuteroxanthene (0.025 g) and the cation (one third to four times the moles of the 9-deuteroxanthene), individually, in two separate vials. Either the cation or the 9-deuteroxanthene or both were dissolved in CD_3CN and the reactants were mixed together.

For the reaction at 0°C, the 9-deuteroxanthene was dissolved in acetonitrile and then introduced into one arm of the flask shown in Figure 1. The triphenylmethyl cation was introduced into the other side-arm.

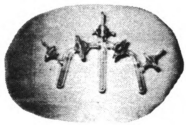
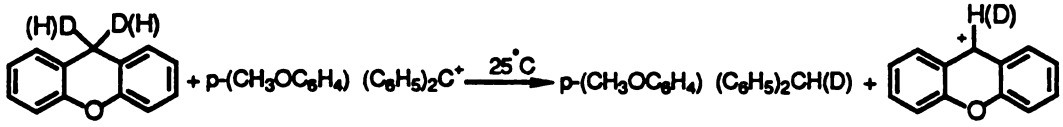


Figure 1. The apparatus which was used for the low temperature reactions.

The arms were then submerged in ice-water for ~20 minutes. At his time the contents of the two arms were mixed together. The flask was kept at 0°C for ~15 minutes and then warmed to room temperature. Spectra were then taken.

The above procedure was used for the reaction of 44°C with an oil bath used to warm the arms of the apparatus.

Reaction of Xanthene with Anisyldiphenylmethyl Tetrafluoroborate (spectra 44-45):

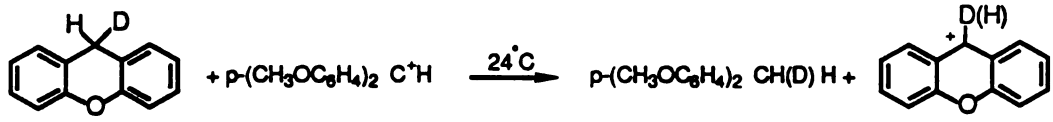


(3) spectra 44-45

For the reaction of xanthene with anisyldiphenylmethyl tetrafluoroborate, equimolar amounts of xanthene and anisyldiphenylmethyl tetrafluoroborate (0.14 mmols) were dissolved individually in 1 ml CD_3CN and the cation solution was transferred to the vial which contained the xanthene solution. The progress of the reaction was monitored by ^1H NMR at 25°C. The reaction of dideuteroxanthene was carried out in the same way.

A small peak appears at 2.1 ppm in the ^1H NMR spectrum of CD_3CN, which disappears when these reactions are carried out in this solvent. Another impurity appears at 3.7 ppm near the methoxy peaks in both experiments

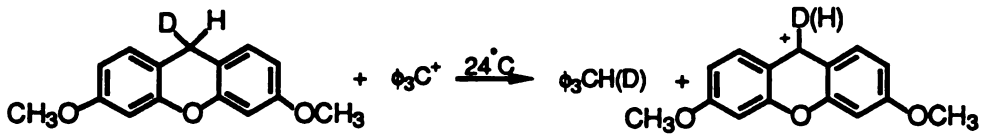
Reaction of 9-Deuteroxanthene with Dianisylmethyl Perchlorate (spectra 37-39, 41-43):



(4) spectra 37-39
spectra 41-43

For the title reaction, the 9-deuteroxanthene (0.025 g) and the dianisylmethyl perchlorate (two and a half times the moles of the 9-deuteroxanthene) were weighed individually in separate vials. Trideuteroacetonitrile (3 ml) was used to dissolve the cation and the reactants were then mixed together.

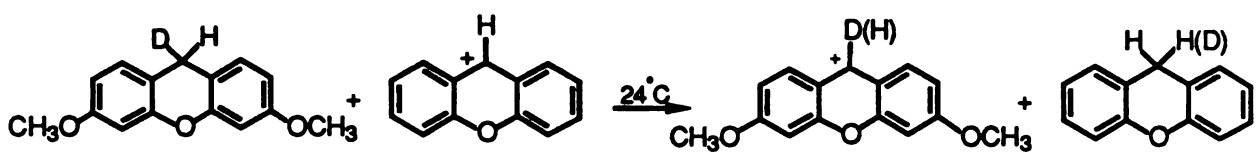
Reaction of 2,6-Dimethoxy-9-deuteroxanthene with Triphenylmethyl Tetrafluoroborate (spectrum 49):



(5) spectrum 49

For the title reaction an excess of the cation (1.3-2.5 times) which was initially dissolved in CD_3CN (0.26-0.5 ml) was added to the solid 2,6-dimethoxy-9-deuteroxanthene (0.0034-0.0048 g).

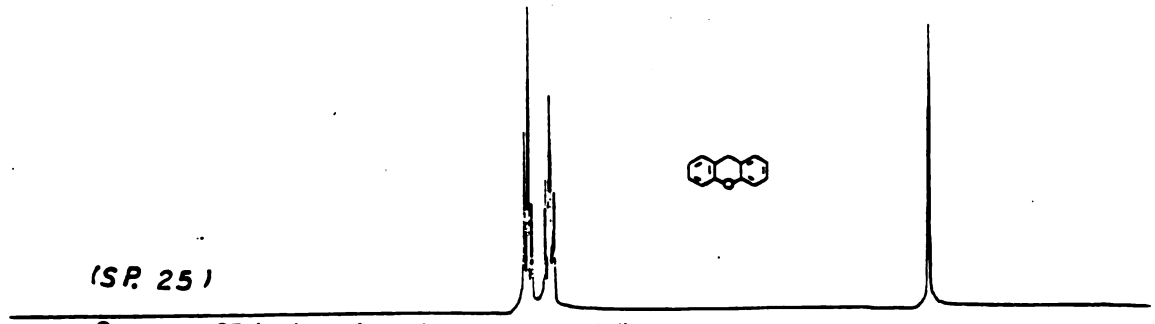
Reaction of 2,6-Dimethoxy-9-deuteroxanthene with 9-Xanthyl Tetrafluoroborate (spectrum 50):



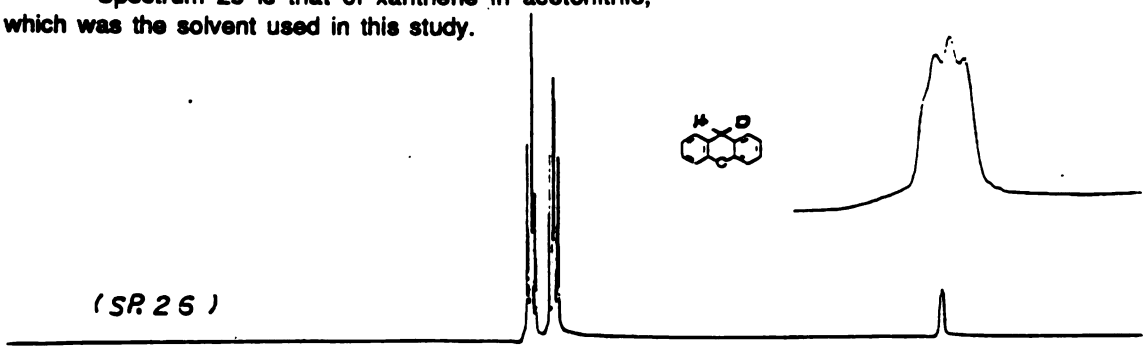
(6) spectrum 50

The title reaction was carried out in the presence of excess 9-xanthyl cation (1.5 to 3 times molar excess). Each of the reactants was dissolved separately, either in the minimum amount of CD_3CN before mixing, or the cation was dissolved in CD_3CN and then added to the solid 2,6-dimethoxy-9-deuteroxanthene. The quantities of the hydrocarbon which were used for each experiment were 0.0023 g to 0.025 g and the CD_3CN from a few drops to 1.5 ml.

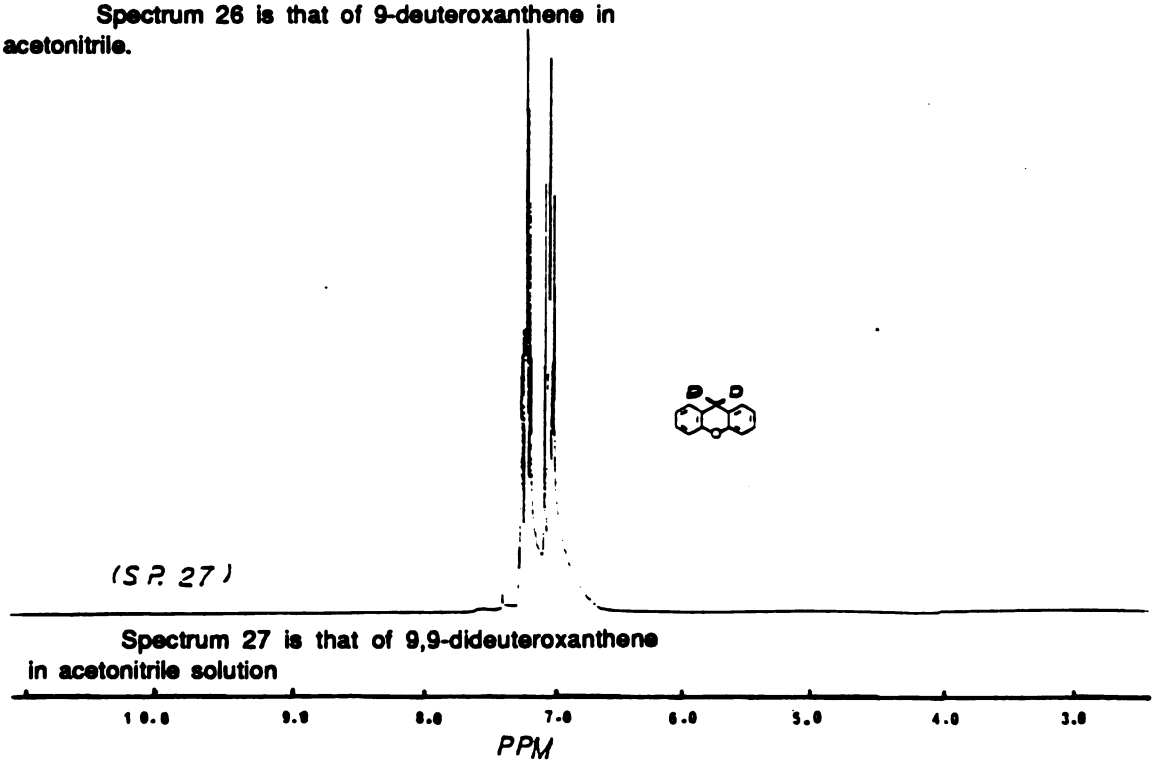
A Bruker 25 MHz spectrometer was used to study all the reactions. Spectra 25-50 are representative of the reactions studied.



Spectrum 25 is that of xanthene in acetonitrile, which was the solvent used in this study.



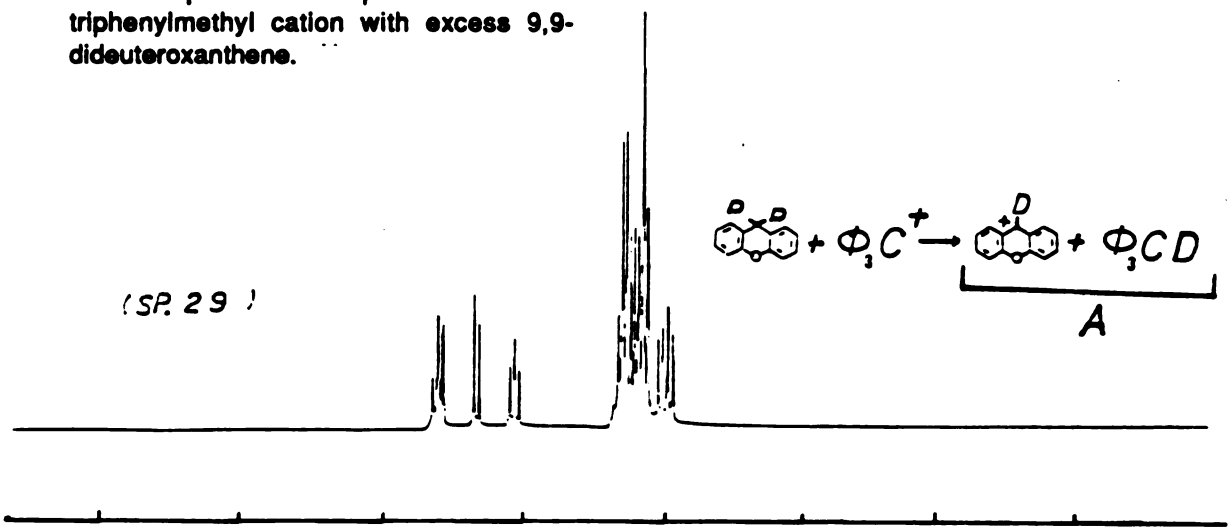
Spectrum 26 is that of 9-deuteroxanthene in acetonitrile.

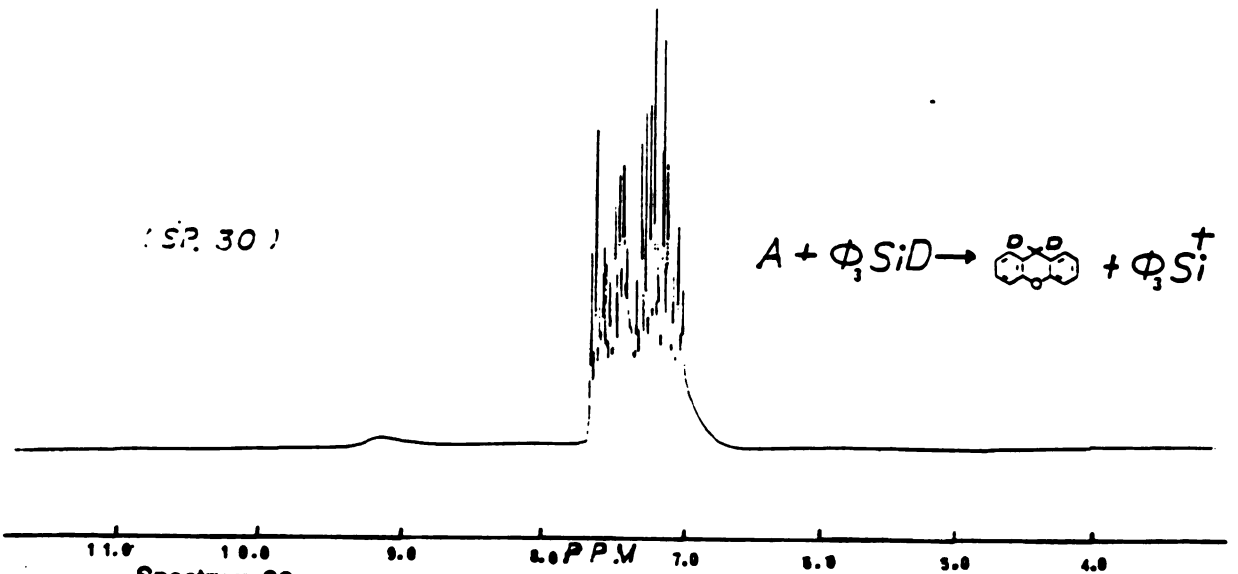


Spectrum 27 is that of 9,9-dideuteroxanthene in acetonitrile solution

Spectrum 28 represents the reaction of equimolar amounts of xanthene and triphenylmethyl tetrafluoroborate.

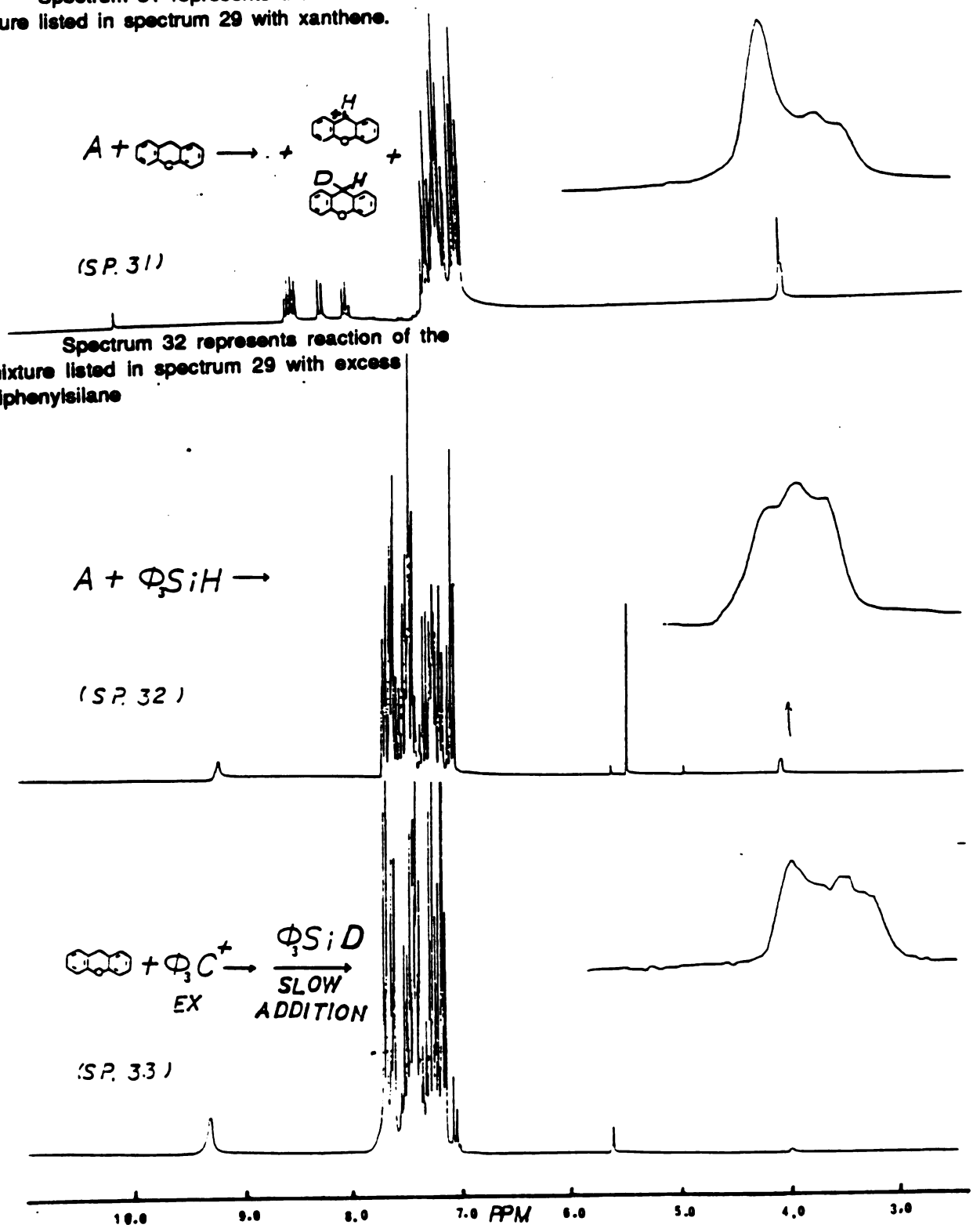
Spectrum 29 represents the reaction of the triphenylmethyl cation with excess 9,9-dideuteroxanthene.





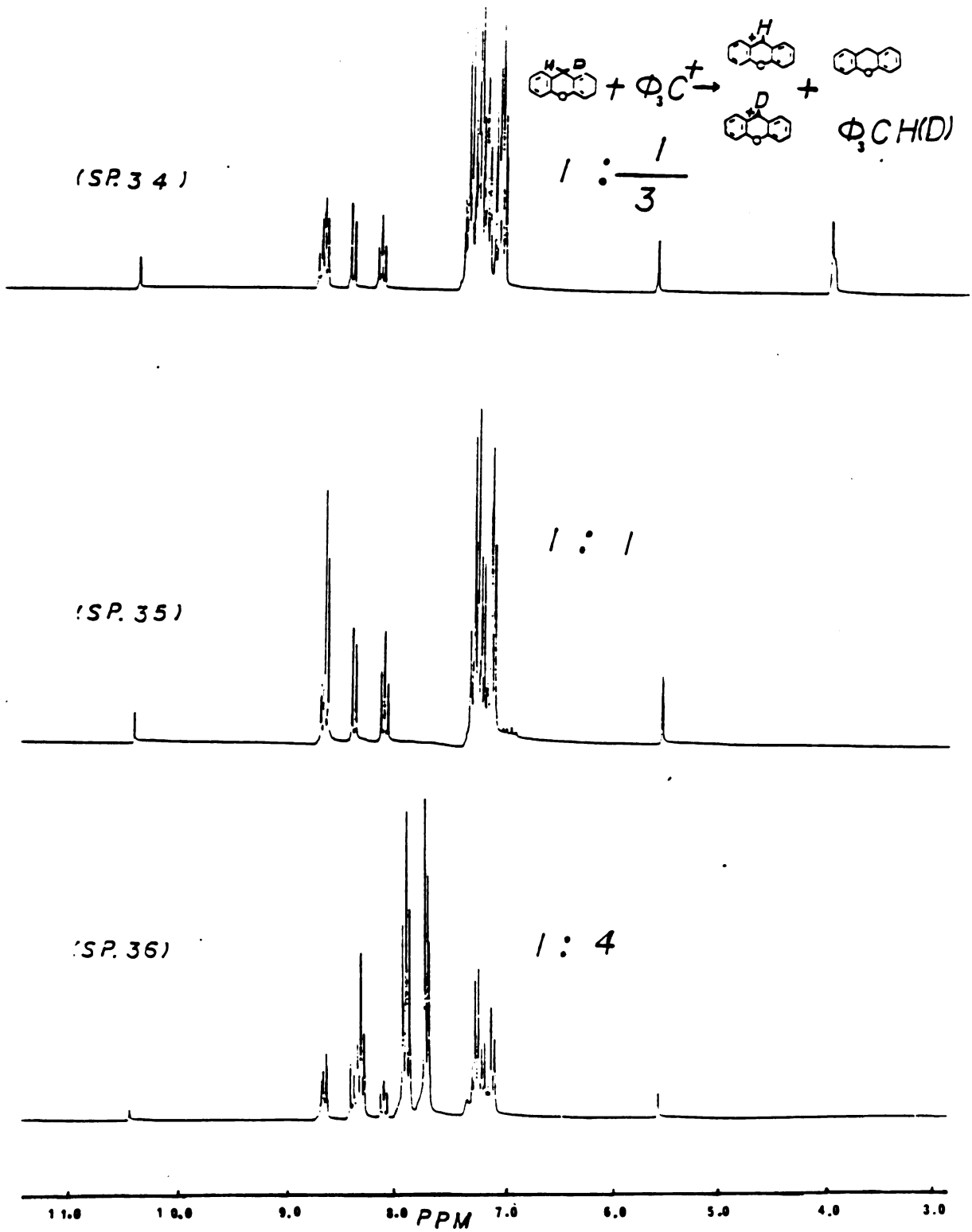
Spectrum 30 represents the reaction of the mixture listed in spectrum 29 with triphenylsilane-1-d. No peak appears at 4.02 ppm.

Spectrum 31 represents the reaction of the mixture listed in spectrum 29 with xanthene.

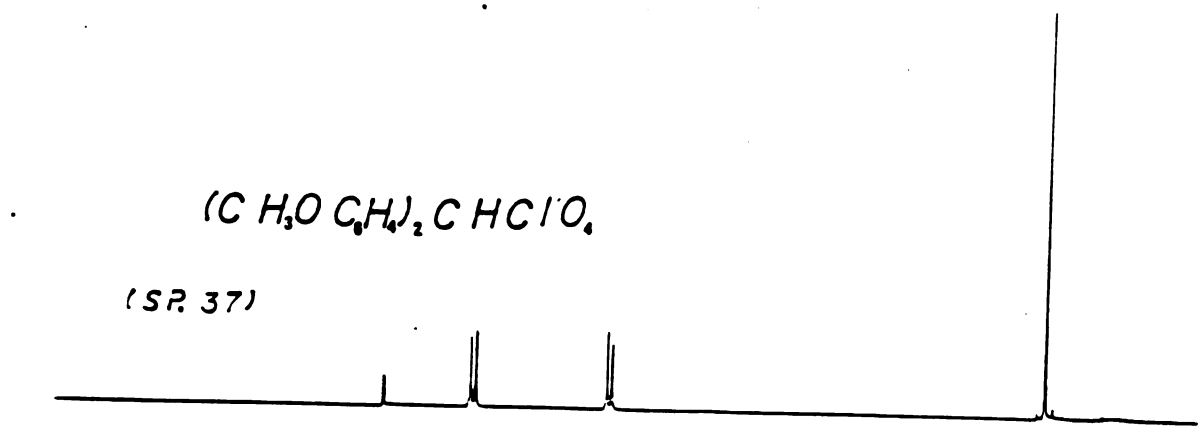


Spectrum 32 represents reaction of the mixture listed in spectrum 29 with excess triphenylsilane

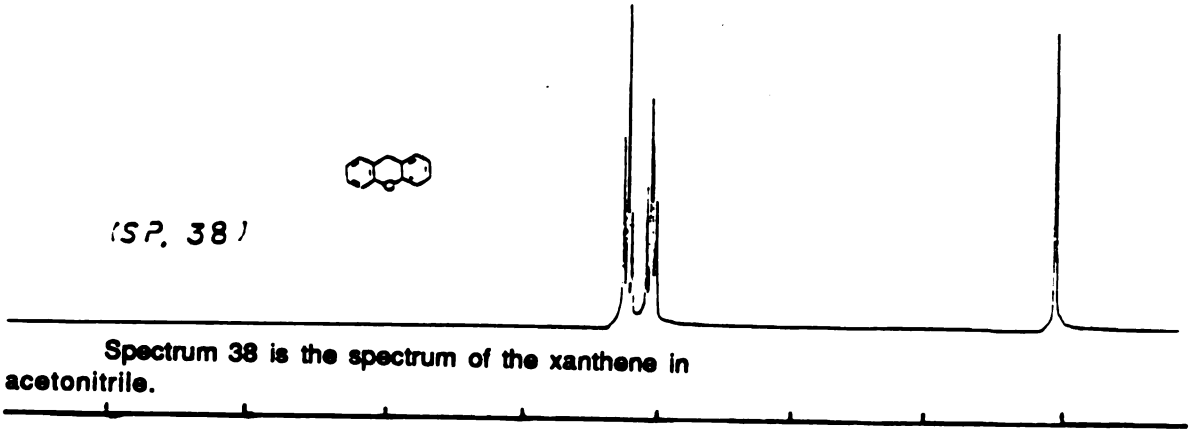
Spectrum 33 represents the reaction resulting from a slow and periodic addition of deuterated triphenylsilane with the reaction mixture of xanthene and triphenylmethyl cation.



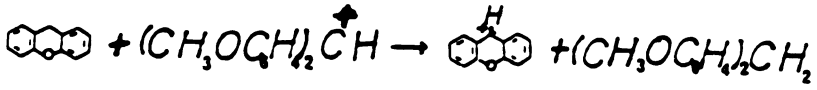
Spectra 34, 35 and 36 represent the reaction of 9-deuteroxanthene with one third, one and four mole excess of triphenylmethyl tetrafluoroborate respectively.



Spectrum 37 is that of of dianisylmethyl perchlorate in acetonitrile.

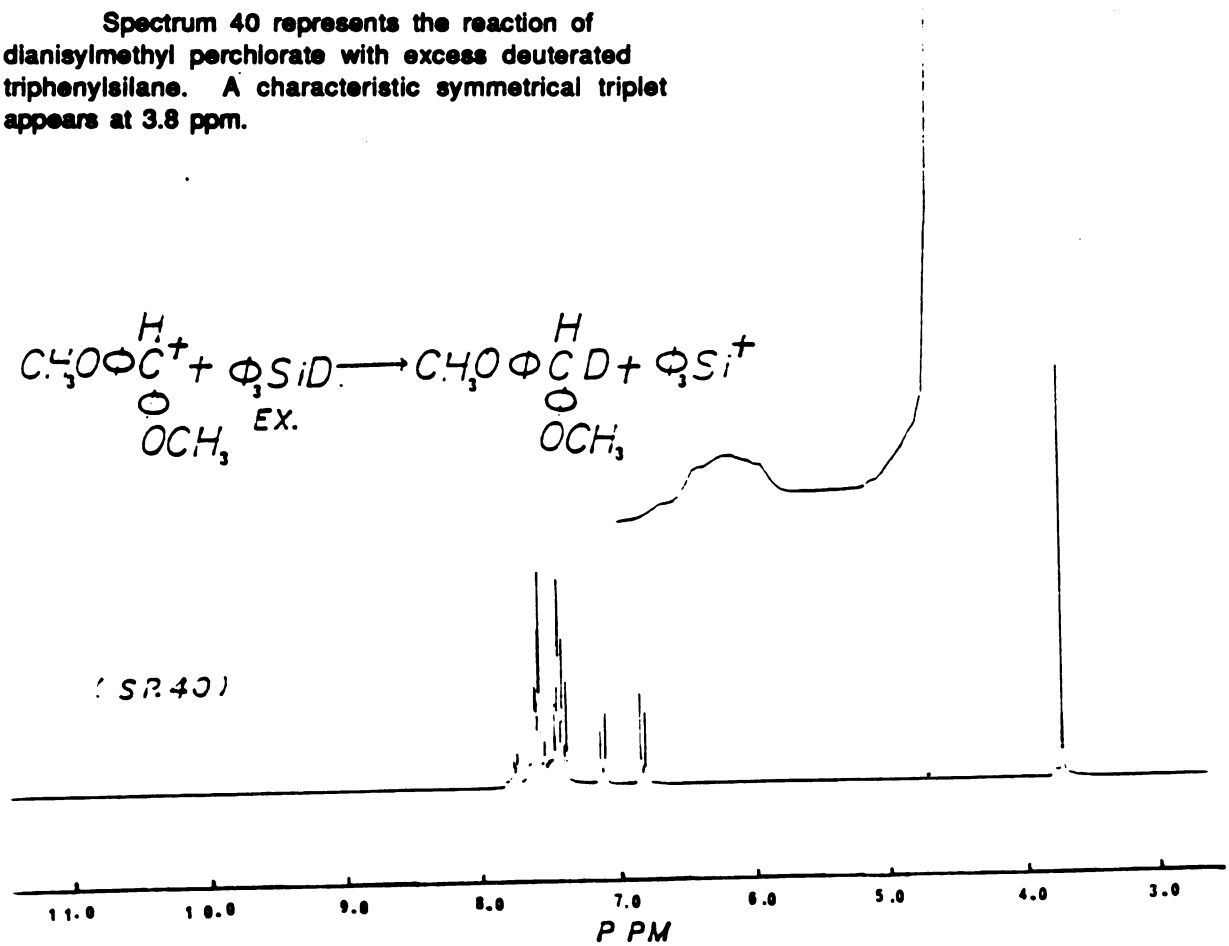


Spectrum 38 is the spectrum of the xanthene in acetonitrile.

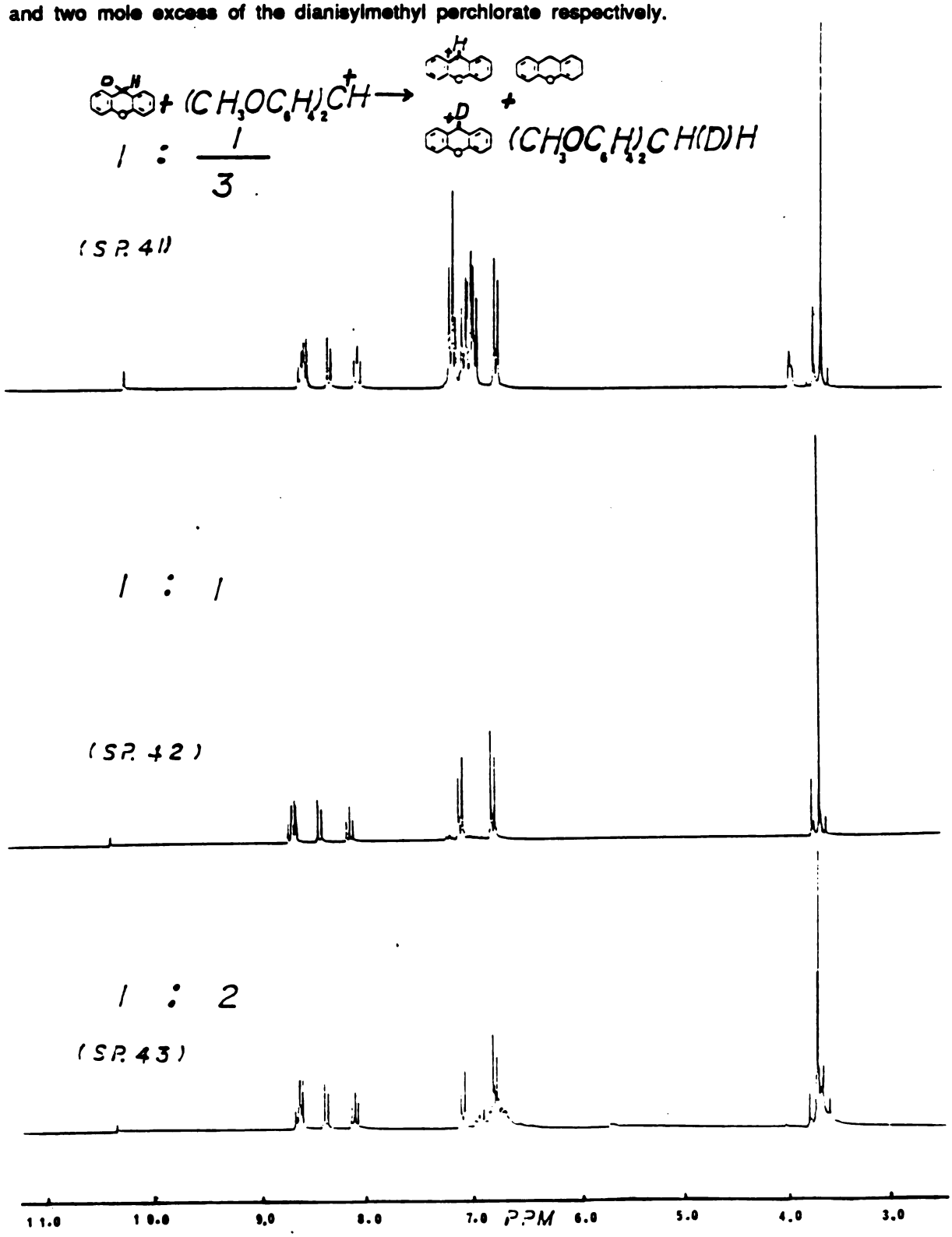


Spectrum 39 represents the reaction of dianisylmethyl perchlorate with excess xanthene.

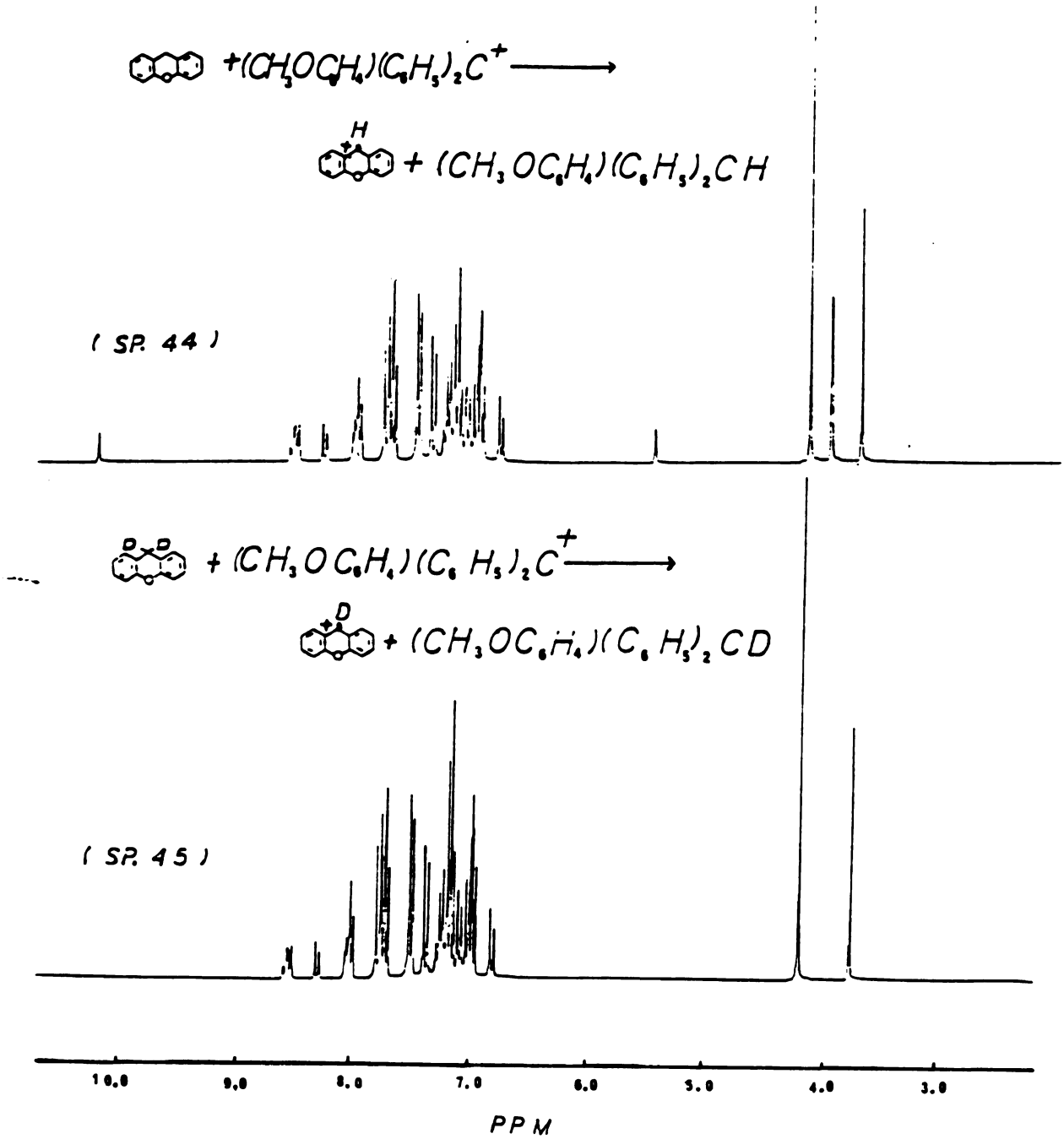
Spectrum 40 represents the reaction of dianisylmethyl perchlorate with excess deuterated triphenylsilane. A characteristic symmetrical triplet appears at 3.8 ppm.



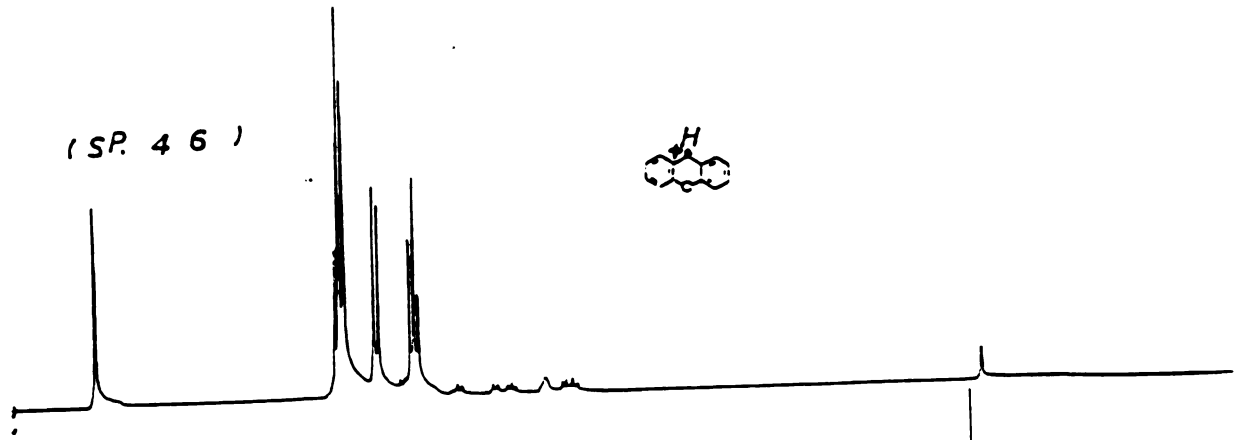
Spectra 41, 42 and 43 represent the reaction of 9-deuteroxanthene with one third, one and two mole excess of the dianisylmethyl perchlorate respectively.



Spectra 44 and 45 represent the reactions of xanthene and 9,9-dideuteroxanthene with anisyldiphenylmethyl tetrafluoroborate respectively.

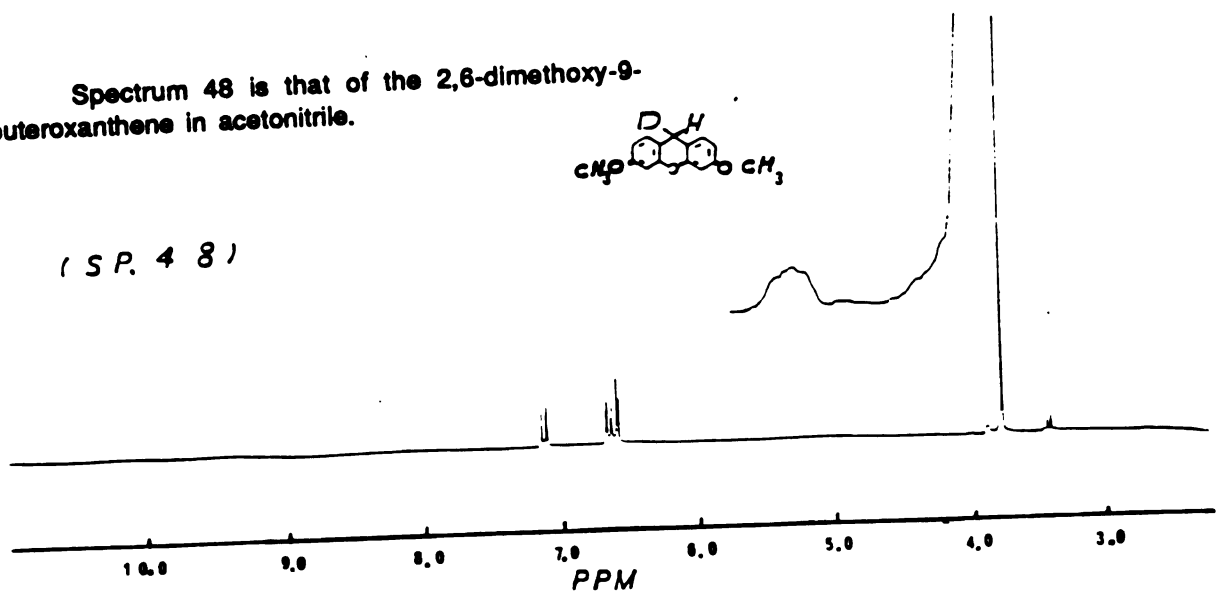


Spectrum 46 represents the xanthyl tetrafluoroborate in acetonitrile solution.

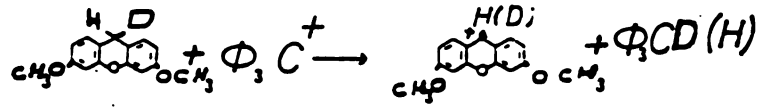


Spectrum 47 is that of 2,6-dimethoxyxanthyl tetrafluoroborate in acetonitrile solution. The singlet

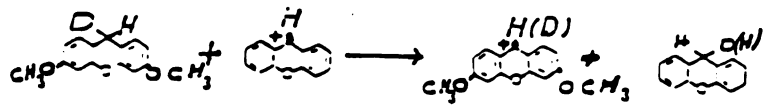
Spectrum 48 is that of the 2,6-dimethoxy-9-deuteroxanthene in acetonitrile.



Spectrum 49 represents the reaction of 2,6-dimethoxy-9-deuteroxanthene with the triphenylmethyl tetrafluoroborate.



Spectrum 50 represents the reaction of 2,6-dimethoxy-9-deuteroxanthene with the xanthyl tetrafluoroborate.



Spectrum 25 is that of xanthene in acetonitrile, which was the solvent used in this study. A singlet due to the hydrogens on carbon 9 appear at 4.02 ppm and two multiplets due to the hydrogens of the aromatic rings appear between 6.6 and 7.3 ppm.

Spectrum 26 is that of 9-deuteroxanthene in acetonitrile. It looks like spectrum 25 but instead of the singlet at 4.02 ppm in spectrum 25, a symmetrical triplet appears at 4.02 ppm characteristic of the hydrogen on carbon-9 split by the deuterium.

Spectrum 27 is that of 9,9-dideuteroxanthene in acetonitrile solution and the only peaks that appear are the two multiplets due to the hydrogens of the aromatic rings between 6.6 and 7.3 ppm. No peak appears at 4.02 ppm.

Spectrum 28 represents the reaction of equimolar amounts of xanthene and triphenylmethyl tetrafluoroborate. The singlet at 5.55 ppm and the multiplet between 8.1-8.4 ppm are due to triphenylmethane. The xanthyl cation shows a singlet at 10.34 ppm, and a multiplet, a duplet and a triplet between 8.0 and 8.8 ppm.

Spectrum 29 represents the reaction of the triphenylmethyl cation with excess 9,9-dideuteroxanthene. No peak appears at 10.34, 5.55 or 4.02 ppm.

Spectrum 30 represents the reaction of the mixture listed in spectrum 29 with triphenylsilane-1-d. No peak appears at 4.02 ppm.

Spectrum 31 represents the reaction of the mixture listed in spectrum 29 with xanthene. A peak at 10.34 ppm and an unsymmetrical triplet at 4.02 ppm appear in the spectrum. (The unsymmetrical triplet at 4.02 ppm is due to the superimposition of the singlet of the xanthene and the symmetrical triplet of the 9-deuteroxanthene).

Spectrum 32 represents reaction of the mixture listed in spectrum 29 with excess triphenylsilane, whose silane hydrogen appears at 5.48 ppm. A symmetrical triplet appears at 4.02 ppm.

Spectrum 33 represents the reaction resulting from a slow and periodic addition of deuterated triphenylsilane with the reaction mixture of xanthene and triphenylmethyl cation. An unsymmetrical triplet appears at 4.02 ppm.

Spectra 34, 35 and 36 represent the reaction of 9-deuteroxanthene with one third, one and four mole excess of triphenylmethyl tetrafluoroborate respectively.

Spectrum 37 is that of of dianisylmethyl perchlorate in acetonitrile. A singlet due to the methoxy groups appears at 4.14 ppm, a singlet due to the methyl hydrogen appears at 8.99 ppm and the AA'BB' hydrogens of the phenyl rings appear in the region 7.3 - 8.3 ppm.

Spectrum 38 is the spectrum of the xanthene in acetonitrile.

Spectrum 39 represents the reaction of dianisylmethyl perchlorate with excess xanthene. In addition to the peaks of the xanthyl cation and xanthene two duplets at 6.8 and 7.1 ppm (AA'BB' pattern) and two singlets at 3.72 (methoxy) and 3.81 (methylene) ppm due to the dianisylmethane are shown also in this spectrum.

Spectrum 40 represents the reaction of dianisylmethyl perchlorate with excess deuterated triphenylsilane. A characteristic symmetrical triplet appears at 3.8 ppm.

Spectra 41, 42 and 43 represent the reaction of 9-deuteroxanthene with one third, one and two mole excess of the dianisylmethyl perchlorate respectively.

Spectra 44 and 45 represent the reactions of xanthene and 9,9-dideuteroxanthene with anisyldiphenylmethyl tetrafluoroborate respectively.

Spectrum 46 represents the xanthyl tetrafluoroborate in acetonitrile solution.

Spectrum 47 is that of 2,6-dimethoxyxanthyl tetrafluoroborate in acetonitrile solution. The singlet at 9.53 ppm is due to the hydrogen on carbon 9; the doublet at 8.2 ppm and the multiple at 7.4 ppm are due to the hydrogens of the phenyl ring; and the singlet at 4.17 ppm is due to the methoxy groups.

Spectrum 48 is that of the 2,6-dimethoxy-9-deuteroxanthene in acetonitrile. The doublet at 7.2 ppm and the multiple at 6.6 ppm are due to the hydrogens of the aromatic rings. The singlet at 3.77 ppm is due to the methoxy groups and the symmetrical triplet, which is characteristic of the hydrogen on carbon 9, appears at 3.9 ppm.

Spectrum 49 represents the reaction of 2,6-dimethoxy-9-deuteroxanthene with the triphenylmethyl tetrafluoroborate.

Spectrum 50 represents the reaction of 2,6-dimethoxy-9-deuteroxanthene with the xanthyl tetrafluoroborate.

RESULTS AND DISCUSSION

Calculations of rate constants and kinetic isotope effects ($^{k}H/^{k}D$):

The kinetic isotope effects for the reactions of xanthenes, except reaction **3**, were calculated from the rates of competitive transfer of hydrogen versus deuterium from the same carbon. Carbon 9 of the xanthene and the substituted xanthenes was the one bearing the hydrogen and deuterium. In this case the isotope effect is given by the ratio of the concentration of hydrogen atoms transfered from carbon 9, versus the concentration of the hydrogen atoms remaining on this carbon. These concentrations correspond to the integrals of the areas the hydrogens signals in the proton NMR..

Because reaction (3) proceeded quite slowly, the isotope effect was calculated from the individual ^{k}H and ^{k}D determinations, which were carried out following the procedure described for the reactions in Section II.

Reaction of 9-Deuteroxanthene with Triphenylmethyl Tetrafluoroborate (1-2):

The average isotope effects were calculated to be 3.1±0.2, 3.4 ± 0.4 and 3.7 ± 0.1 at 44°C, 24°C and 0°C respectively. They were determined from the ratio of the area under the peak at 5.56 ppm and the area under the peak at 10.34 ppm.

Table 1 shows the $^{k}H/^{k}D$ for this reaction, determined under different conditions.

Table 1. The dependence of the $^{k}H/^{k}D$ on the ratio of the concentrationof 9-deuteroxanthene and triphenylmethyl tetrafluoroborate at different temperatures.

Entry	°C	concentration ratios (9-deuteroxanthene/ triphenylmethyl cation)	$^{k}H/^{k}D$
1[a]	24.0±0.5	1:0.33	1.94
2[a]	24.0±0.5	1:0.50	2.30
3[a]	24.0±0.5	1:0.66	2.37
4[a]	24.0±0.5	1:1.00	2.97
5[a]	24.0±0.5	1:1.00	2.65
6[a]	24.0±0.5	1:2.00	2.98
7[a]	24.0±0.5	1:3.00	3.35
8[a]	24.0±0.5	1:4.00	3.11
9[a,b]	24.0±0.5	1:4.00	3.88
10[c]	24.0±0.5	1:4.00	3.37
11[d]	24.0±0.5	1.4.00	3.36
12[e]	24.0±0.5	1:4.00	3.12
13[e]	0.0±0.5	1:4.00	3.78
14[e]	0 0±0.5	1:2.00	3.65
15[e]	44.0±0.5	1:4.00	3.38
15[e]	44.0±0.5	1:4.00	2.93

[a] A solution of triphenylmethyl tetrafluoroborate in CD_3CN (1 ml) was added to the solid 9-deuteroxanthene (0.025 g).

[b] Reaction 9 was also followed for 1.5 hr at intervals of 30 minutes. $^{k}H/^{k}D$ values were 3.82, 3.89, and 3.93.

[c] A solution of 9-deuteroxanthene in CD_3CN (1 ml) was added to solid triphenylmethyl tetrafluoroborate.

[d] A solution of triphenylmethyl tetrafluoroborate in CD_3CN (1 ml) was added to the solution of xanthene in CD_3CN (1 ml).

[e] A solution of xanthene in CD_3CN (1 ml) was added to the solution of triphenylmethyl tetrafluoroborate in CD_3CN (1 ml).

The $^{k}H/^{k}D$ isotope effects were determined by dividing the area under the signal at 5.56 ppm due to the methine proton of triphenylmethane by the area under the signal at 10.34 ppm due to the methine proton of the xanthyl cation.

All the reactions of xanthene, 9-deuteroxanthene and 9,9-dideuteroxanthene with triphenylmethyl tetrafluoroborate were studied in acetonitrile. All of them were extremely fast.

The following observations and comments can be made:

a) When the 9-deuteroxanthyl cation, generated from the triphenylmethyl cation and 9,9-dideuteroxanthene *in situ*, was reacted with triphenylsilane-1-d(Φ_3Si-D), the only product observed was 9,9-dideuteroxanthene. Therefore, the only carbocationic center reacting is the C-9 (sp. 29-30).

b) When the 9-deuteroxanthyl cation was reacted with xanthene, a proton peak appeared at 10.34 ppm (sp. 31) that is assigned to the 9-xanthyl cation. This finding establishes the xanthene-xanthyl cation equilibrium in solution.

c) In the reaction of the xanthyl cation with triphenylsilane (slow and periodic addition of the silane), an unsymmetrical triplet appeared at 4.02 ppm (sp. 33). This signal was duplicated in the ^{1}H NMR of a mixture of xanthene and 9-deuteroxanthene, indicating that both species are present in the carbocation reaction.

d) When the 9-deuteroxanthyl cation was reacted with triphenylsilane (fast addition of the silane), only a symmetrical triplet was observed at 4.02 ppm (sp. 32).

e) The above independent reactions show that the identity equilibrium between xanthene and the 9-xanthyl cation occurs quite easily. In order to eliminate this equilibrium which complicates the determination of $^kH/^kD$, the ratio of triphenylmethyl cation xanthene was varied. It was found that a 3-4 times excess of triphenylmethyl cation over xanthene gave reasonably constant $^kH/^kD$ values (Table 1).

Reaction of Xanthene with Anisyldiphenylmethyl Tetrafluoroborate (3):

Because the reaction between xanthene and anisyldiphenylmethyl tetrafluoroborate proceeded slowly, the rate constants ^{k}H and ^{k}D were calculated separately (by using the program which appears in the appendix, pages 94-95) and found to be $(4.14\pm0.10)\times10^{-3}$ and $(6.48\pm0.07)\times10^{-4}$, respectively (appendix, pages 120-121). The progress of the reaction was followed by monitoring the methoxy peaks of the product and the reactant (sp. 44-45). The isotope effect for this reaction was calculated to be 6.4±0.2 at 25°C (appendix, pages 141).

When equimolar amounts of xanthene and anisyldiphenylmethyl tetrafluoroborate (0.14 mmoles) were dissolved in CD_3CN (2.0 ml) and the progress of the reaction was monitored by ^{1}H NMR at 25°C, in 1/2 hour the reaction was 32% completed and an equal amount of each product was formed, as shown by the same integral for the peaks at 5.6 ppm and 10.5 ppm, with no indication of decomposition or by-products. The reaction of dideuteroxanthene which was carried out as above took 172 minutes to arrive at 32% completion. The percent reaction completion after 50 minutes was 44.3% for the xanthene and 12.7% for the dideuteroxanthene.

Reaction of 9-Deuteroxanthene with Dianisylmethyl Perchlorate (4):

The isotope effects determined for the reactions of xanthene with dianisylmethyl perchlorate cover a wide range because of significant errors involved in the integration of various peak signals. Table 2 summarizes the integration values for the various xanthyl cation protons in the reaction of 9-deuteroxanthene with dianisylmethyl perchlorate.

Table 2. Integration values of the xanthyl cation protons in the reaction of 9-deuteroxanthene with dianisylmethyl perchlorate

Entry	Concentration ratio*	Time sec	10.3 ppm (1H)[a]	8.7 ppm (4H)[b]	8.4 ppm (2H)[b]	8.1 ppm (2H)[b]
1	1:2.5	$1.8x10^3$	0.420	7.257	3.493	3.739
		$3.6x10^3$	0.479	6.991	3.507	3.625
		$5.4x10^3$	0.457	6.759	3.392	3.509

* Ratio of 9-deuteroxanthene : dianisylmethyl perchlorate.
[a] Xanthyl cation methine hydrogen.
[b] Xanthyl cation phenyl ring hydrogens.

Table 3 below summarizes the integration values for the various xanthyl cation protons in the reaction of 9-deuteroxanthene with triphenylmethyl tetrafluoroborate (reaction 10, Table 1).

Table 3. Integration values of the xanthyl cation protons in the reaction of 9-deuteroxanthene with triphenylmethyl tetrafluoroborate (Reaction 10, Table 1).

Entry	Concentration ratio**	10.3 ppm (1H)[c]	8.7 ppm (4H)[d]	8.4 ppm (2H)[d]	8.1 ppm (2H)[d]	5.4 ppm (1H)[e]
1	1:4	0.491	8.393	4.595	4.154	1.653

** Ratio of 9-deuteroxanthene : triphenylmethyl tetrafluoroborate.
[c] Xanthyl cation methine hydrogen.
[d] Xanthyl cation phenyl ring hydrogens.
[e] Triphenylmethane methine hydrogen.

Comparison of the data summarized in Tables 2 and 3 reveals that the isotopic effects of the two reactions are quite similar. Unfortunately, precise measurements of the primary isotope effects was difficult due to secondary isotopic effects and significant errors involved in the integration of the xanthyl cation multiple peaks. Table 4 presents the integration data of the protons of 9-xanthyl tetrafluoroborate in CD_3CN solution.

Table 4. Integration data of the xanthyl cation protons (solution of 9-xanthyl tetrafluoroborate in deuteroacetonitrile).

10.3 ppm (1H)[a]	8.7 ppm (4H)[b]	8.4 ppm (2H)[b]	8.1 ppm (2H)[b]
10.573 10.764	53.288	25.311	26.679

[a] Xanthyl cation methine hydrogen.
[b] Xanthyl cation phenyl ring hydrogens.

Table 2 demonstrates that the integration ratio of the xanthyl hydrogen at C-9 with respect to the other xanthyl protons changes with time.

The above limitations notwithstanding, one may make the following comments regarding the reactions of dianisylmethyl perchlorate with xanthene (sp. 37-39) and 9-deuteroxanthene (sp. 41-43).

a) As observed in reaction (1), also in this reaction, varying the amount of carbocation with respect to that of 9-deuteroxanthene resulted in different ratios of the xanthyl cations formed (sp. 41-43). Spectrum 42 represents the reaction of equimolar quantities of both xanthene and dianisylmethyl perchlorate. It shows that the only reaction occurring is the isotope exchange between the methine carbon of the cation and the xanthene C-9 hydrogens, and that no new carbon-carbon bond or any other by-products are formed.

b) Reaction of the cation with deuterated triphenylsilane gives a symmetrical triplet at 3.8 ppm (sp. 40).

c) The solid cation is stable for 1-2 hours at room temperature and for a few days if it is refrigerated. However, a solution of the cation in CD_3CN decomposes in a matter of 30 minutes (sp. 43).

d) Reaction of dianisylmethane (commercial) with its cation counterpart results in a black solution. The NMR spectrum of this solution indicates that decomposition has occurred.

Reaction of 2,6-Dimethoxy-9-deuteroxanthene with Triphenylmethyl Tetrafluoroborate (5):

Table 5 summarizes the isotope effects calculated from integration of the various protons (sp. 49). The average isotope effect for this reaction is $^{k}H/^{k}D = 5.4 \pm 0.5$.

Table 5. Isotope effects for the reaction of 2,6-dimethoxy-9-deuteroxanthene with triphenylmethyl tetrafluoroborate.

Entry*	$^{k}H/^{k}D$ 8.294[a] vs 9.530[d] ppm	$^{k}H/^{k}D$ 8.258[a] vs 9.530[d] ppm	$^{k}H/^{k}D$ 8.301-8.247[a] vs 9.530[d] ppm	$^{k}H/^{k}D$ 5.582[b] vs 9.530[d] ppm	$^{k}H/^{k}D$ 4.167[c] vs 9.530[d] ppm
1a				4.91	5.28
1b				4.91	
1c				6.22	4.99
1d					5.59
2a	5.58	5.28	5.74	5.35	
2b	5.25	4.74		5.38	
2c	5.58	5.11		5.35	
2d					5.87
3a	5.20	6.06	5.70		5.89
3b					5.91

* Three reactions were run 1, 2 and 3. 1a, 1b, 1c, 1d give the isotope effects which were calculated from different integrations on the same sample. The same is true for 2a, 2b, 2c, and for 3a, 3b.

[a] Integration of the 2,6-dimethoxyxanthyl cation phenyl hydrogens.

[b] Integration of the triphenylmethane methine hydrogen.

[c] Integration of the 2,6-dimethoxyxanthyl cation methoxy hydrogens.

[d] Integration of the 2,6-dimethoxyxanthyl cation methine ring hydrogens.

Since this reaction proceeded at a fast rate, an excess of the cation (1.3-2.5 times) was used. Entry 1 represents the data for the reaction in which the cation was initially dissolved in CD_3CN, in order to consume the species represented by the peak at 2.1 ppm in the solvent, followed by the addition of this solution to solid 2,2-dimethoxy-9-deuteroxanthene. Computation of the $^{k}H/^{k}D$ for this reaction was troublesome if the

C-9 proton of the xanthyl cation is integrated with respect to the remaining aromatic protons of the xanthyl cation, because of the proximity of the latter with those of the triphenylmethyl cation. However, the former proton may be compared accurately with either the triphenylmethane proton (5.58 ppm) or the OCH_3 protons of xanthene at 4.17 ppm.

Entries 2 and 3 represent the same reaction condition as that on entry 1, without an excess of the cation present. Thus, in this case, the xanthyl cation aromatic protons may also be used for the computation of $^{k}H/^{k}D$. The values shown in Table 5 have been corrected for errors in integration based on the data in Table 6, which are the integration values of the protons of pure 2,6-dimethoxyxanthyl tetrafluoroborate.

Table 6. Integration of the 2,6-dimethoxyxanthyl tetrafluoroborate protons in CD_3CN solution.

9.530 (1H)[a] ppm	8.294 (1H)[b] ppm	8.258 (1H)[b] ppm	8.301-8.241 (2H)[b] ppm	4.167 (6H)[c] ppm
1.885	1.902	1.967	4.274	13.453

[a] 2,6-dimethoxyxanthyl cation methine hydrogen.
[b] 2,6-dimethoxyxanthyl cation phenyl ring hydrogen.
[c] 2,6-dimethoxyxanthyl cation methoxy hydrogens.

Reaction of 2,6-Dimethoxy-9-deuteroxanthene with Xanthyl Tetrafluoroborate (6):

The kinetic isotope effects of the reaction of 2,6-dimethoxy-9-deuteroxanthene with xanthyl tetrafluoroborate are summarized in Table 7. Because of substantial errors involved in the integration of the small C-9 protons of the 2,6-dimethoxyxanthyl cation and the multiplicity of the other aromatic hydrogens, the computed isotope effects vary greatly.

Table 7. Isotope effects* for the reaction of 2,6-dimethoxy-9-deuteroxanthene with 9-xanthyl cation.

Entry**	Temperature °C	k_H/k_D 8.294[a] vs 9.530[c] ppm	k_H/k_D 8.258[a] vs 9.530[c] ppm	k_H/k_D 8.301-8.214[a] vs 9.530[c] ppm	k_H/k_D 4.167[b] vs 9.530[c] ppm
1a	24.0±0.5	4.40	4.75	4.74	4.60
2a	24.0±0.5	7.57		8.90	
2b	24.0±0.5	5.24	6.86		
2c	24.0±0.5	7.57			8.85
3a	24.0±0.5	8.42	9.45		
3b	24.0±0.5	8.42	8.53		
4a	24.0±0.5	9.03	10.04	10.49	11.37
4b	24.0±0.5	7.85	9.16	7.85	8.57
5a	24.0±0.5	7.41	8.11	8.31	9.08
5b	24.0±0.5	4.63	5.96	5.16	5.72
6a	24.0±0.5				4.26
7a	0.0±0.5	3.65	4.04	3.74	3.84

* The isotope effects shown in this Table have been corrected for errors in integration based on the data in Table 6, which are the integration values of the protons of pure 2,6-dimethoxyxanthyl tetrafluoroborate.

** Seven reactions were run 1, 2, 3, 4, 5, 6, and 7. The isotope effects calculated from different integrations on the same sample are denoted by a, b, or c.

[a] Integration of the 2,6-dimethoxyxanthyl cation phenyl hydrogens.

[b] Integration of the 2,6-dimethoxyxanthyl cation methoxy hydrogens.

[c] Integration of the 2,6-dimethoxyxanthyl cation methine hydrogen.

This reaction was carried out in the presence of excess of the 9-xanthyl cation (1.5 to 3 times molar excess). However, as the cation concentration increased, so did the errors associated with integration, because of the interference of the nearby peaks of the cation. All entries in Table 7 involve reactions where each of the two reactants was separately dissolved in the minimum amount of solvent before mixing, except entries 4 and 5 where the cation was first dissolved in CD_3CN, and then added to the solid 2,6-dimethoxy-9-deuteroxanthene.

Search of possible hydride attack on carbons other than C-9 of the 9-xanthyl cation.

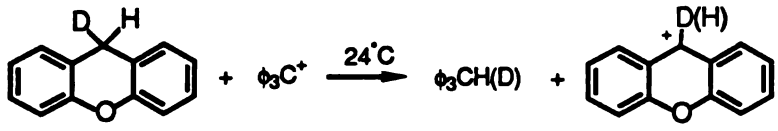
As already discussed, when 9-deuteroxanthyl tetrafluoroborate was treated with the hydride donor triphenylsilane, the NMR spectra of the reaction (sp. 32) showed only a symmetrical triplet at 4.02 ppm. Furthermore, when 9-deuteroxanthyl tetrafluoroborate was reacted with the deuteride donor triphenylsilane-1-d (ϕ_3Si-D), no peak was detected at 4.02 ppm (sp. 30). These experiments exclude the possibility of hydride attack on one of the carbons of the 9-xanthyl cation (other than C-9) with subsequent hydride rearrangement to the C-9 carbon.

During the preparation of 2,6-dimethoxy-9-deuteroxanthene in ether, an excess of lithium aluminum deuteride was added to the suspended yellow solid 2,6-dimethoxyxanthyl tetrafluoroborate. The spectrum of the compound (sp. 48) showed only the symmetrical triplet at 3.88 ppm. Again, this finding excludes attack of hydride on one of the carbons of the 2,6-dimethoxyxanthyl tetrafluoroborate (other than C-9) with subsequent hydride rearrangment to the C-9 carbon.

Again, the spectrum from the reaction of dianisylmethyl perchlorate with the deuterated triphenylsilane (sp. 40) shows only the symmetrical triplet at 4.02 ppm.

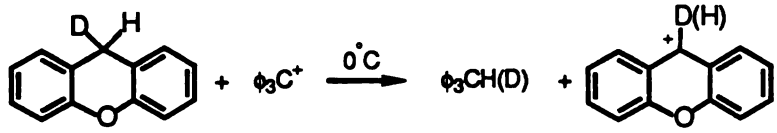
Thus, the product formed is the one expected for deuterium transfer from the silane to the carbon bearing the two aromatic rings and the hydrogen.

Summary of the isotope effects for the reactions in this section:



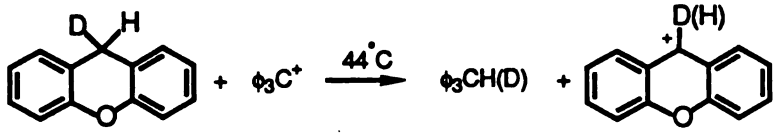
(1)

kH/kD = 3.4 ± 0.4



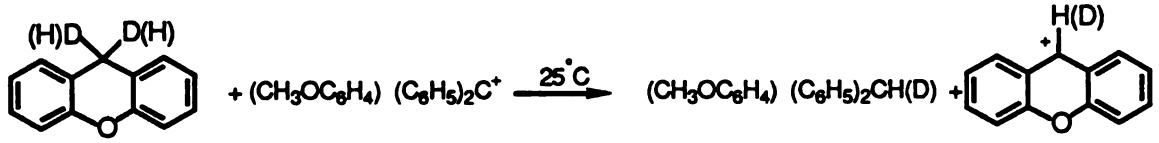
(2a)

kH/kD = 3.7 ± 0.1



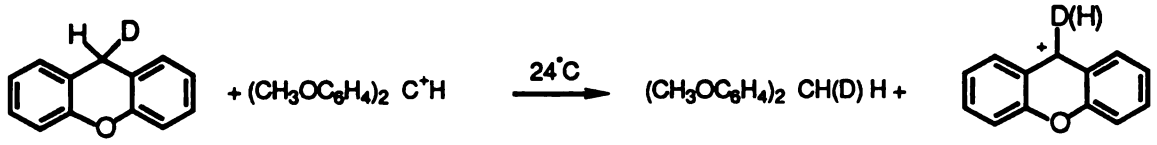
(2b)

kH/kD = 3.1 ± 0.2



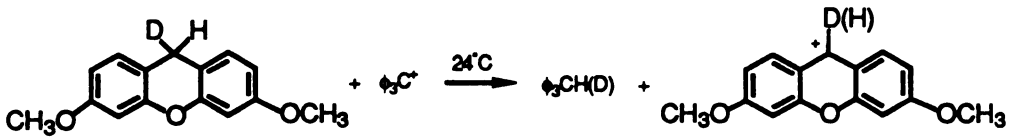
(3)

kH/kD = 6.4 ± 0.2



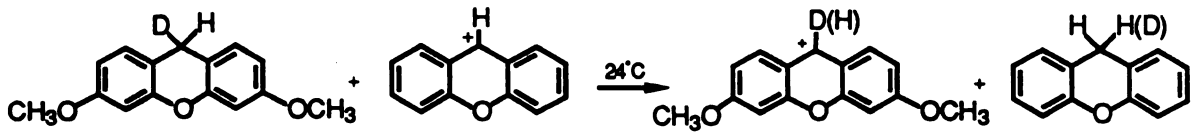
(4)

Isotope effect is nearly the same as reaction (1) but not identified precisely.



(5)

kH/kD = 5.4 ± 0.5



(6)

Isotope effect is large but not precisely identified.

Conclusions

All the reactions studied in this section are consonant with a one-step hydride transfer from the donor hydrocarbon to the acceptor carbocation. These reactions proceed with large kinetic isotope effects, which place them in the range assigned by O'Ferral to cases where the angle between donor-hydrogen-acceptor is 120°-150°, on the assumption that the force constant on either side of the hydrogen is the same. It is also possible that the transition state is linear with unequal force constants on either side of the hydrogen.

The isotope effect of the triphenylmethyl cation with xanthene (3.4±0.4) is smaller than the one of the same cation with the dimethoxy substituted xanthene (5.4 ±0.5). A possible explanation for this finding may be a more symmetrical transition state of the latter reaction that has more similar force constants. The same explanation may apply for the isotope effect of the former reaction which is smaller than the isotope effect of the same hydrocarbon and the anisyldiphenylmethyl tetrafluoroborate (6.4±0.2).

The identity reaction between xanthene and the 9-xanthyl cation is quite fast compared with the corresponding reaction of triphenylmethane and the triphenylmethyl cation (Chapter II).

Investigations of the xanthyl and 2,6-dimethoxyxanthyl cation reactions confirm that the only cationic reacting center present in these cations, under the conditions of this study, is carbon-9. The possibility fo hydride attack on one of the carbons of the xanthyl or the 2,6-dimethoxyxanthyl cation (other than C-9) followed by rearrangement of hydride to the C-9 does not occur. Again the reactions of the dianisylmethyl perchlorate confirm that the only cationic reacting center in this cation is the carbon bearing the two phenyl rings and the hydrogen.

CHAPTER IV

TRIPHENYLSILANE REACTIONS

EXPERIMENTAL

I Preparations

Triphenylsilane and Triphenylsilane-1-D:

The title compounds were prepared[17,18] by reduction of the corresponding chloride (commercial), like in Chapter II, with lithium aluminum hydride and lithium aluminum deuteride respectively, and purified by vacuum distillation.

Trianisylmethyl Cation[15]:

When trianisylmethanol (6 g) was treated with tetraflouroboric acid (4.6 ml, 48% aqueous solution) in propionic anhydride (45 ml), crystals of trianisylmethyl tetrafluoroborate formed immediately. The salt was filtered under argon and washed with petroleum ether (B.P. 35-60°C). The crystals, because of the fast crystallization, contained a very small amount of propionic anhydride.

II. Reactions studied

Triphenylmethyl cation reaction (spectrum 51):

$\phi_3SiH + \phi_3SiD + \phi_3C^+ \longrightarrow {}^*\phi_3Si^+ + \phi_3CH(D)$ (1) spectrum 51

The reactions of triphenylmethyl tetrafluoroborate with the triphenylsilanes were carried out twice. In the first run an equimolar amount of triphenylsilane (0.568 mmol) and its deuterated derivative dissolved inCD_3CN (1 ml) was added to an equimolar amount of solid triphenylmethyl tetrafluoroborate (0.568 mmol). In the second run an equimolar amount of the silane compounds (0.571 mmol) dissolved in CD_3CN (1 ml)

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* ϕ_3Si^+ decomposed.

was added to an equimolar amount of the cation dissolved in CD_3CN (1 ml). The reaction was also performed at -20°C by using the apparatus depicted in Figure 1 (page 48). For this reaction 0.585 mmol of each silane compound in CD_3CN (1 ml) and an equimolar solution of the cation (0.585 mmol) in CD_3CN (1 ml) was used.

Anisyldiphenylmethyl cation reaction (spectrum 52):

$$\phi_3SiH + \phi_3SiD + p\text{-}(CH_3OC_6H_4)(C_6H_5)_2C^+ \longrightarrow {}^*\phi_3Si^+ + p\text{-}(CH_3OC_6H_4)(C_6H_5)_2CH(D) \quad (2)$$ spectrum 52

The reactions of anisyldiphenylmethyl tetrafluoroborate with triphenylsilanes were performed twice. In the first experiment, equimolar amounts of each component (0.693 mmol) dissolved in CD_3CN (2 ml) were added to solid cation (0.693 mmol). In the second experiment, anisyldiphenylmethyl tetrafluoroborate (0.675 mmol) dissolved in CD_3CN (1 ml) was added to a solution of equimolar amounts of each silane compound (0.675 mmol) dissolved in CD_3CN (1 ml).

Trianisylmethyl cation reaction (spectrum 53):

$$\phi_3SiH(D) + p\text{-}(CH_3OC_6H_4)_3C^+ \longrightarrow {}^*\phi_3Si^+ + p\text{-}(CH_3OC_6H_4)_3CH(D) \quad (3)$$ spectrum 53

For the reaction of trianisylmethyl tetrafluoroborate with triphenylsilanes, the cation (0.581 mmol) in 2 ml CD_3CN was added to equimolar amounts of triphenylsilane and its silyl deuterated derivative (0.581 mmol) dissolved in CD_3CN (2 ml).

In a different experiment, trianisylmethyl tetrafluoroborate (0.389 mmol) in 2 ml CD_3CN was added to an equimolar amount of triphenylsilane in 4 ml CD_3CN at 25°C. The reaction of deuterated triphenylsilane with the cation was similar.

---

* ϕ_3Si^+ decomposed.

Reaction of Triphenylmethyl Tetrafluoroborate with Silyl Deuterated Triphenylsilane (spectrum 54):

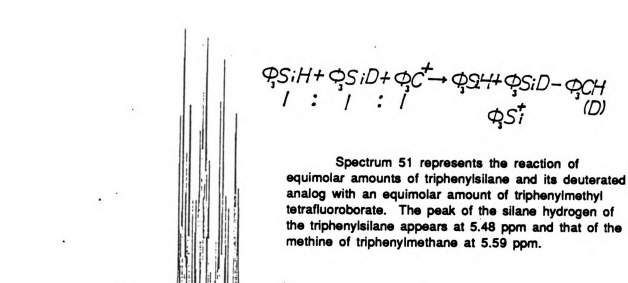
$\phi_3SiD + \phi_3C^+ \longrightarrow {}^*\phi_3Si^+ + \phi_3CD$ (4) spectrum 54

The reaction of triphenylmethyl tetrafluoroborate with silyl deuterated triphenylsilane was carried out with 0.247 mmol of the cation and excess triphenylsilane-1-d (0.280 mmol) in 1 ml CD_3CN.

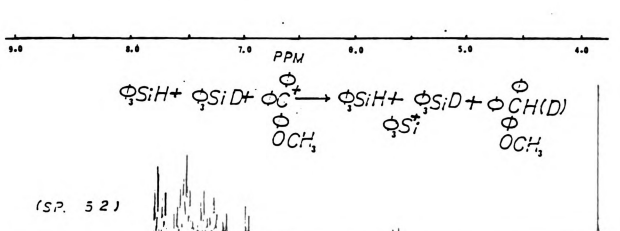
A Bruker 250 MHz NMR instrument was used to study all the reactions. The following spectra 51-54 are representative of the reactions studied:

---

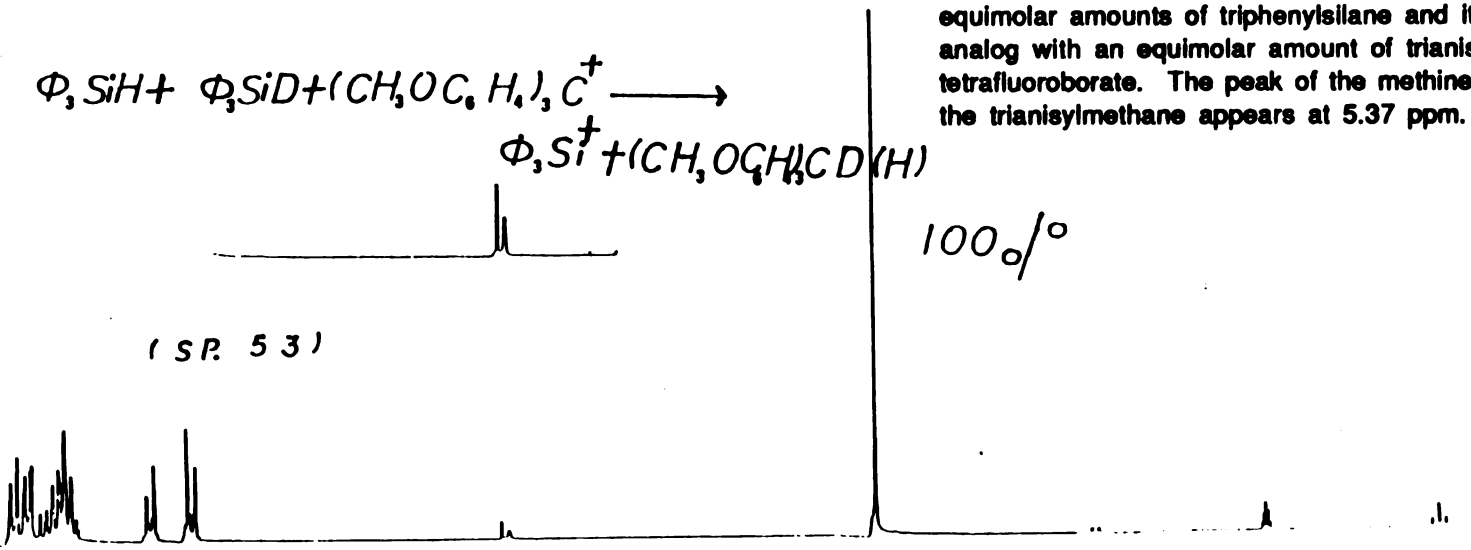
* ϕ_3Si^+ decomposed.



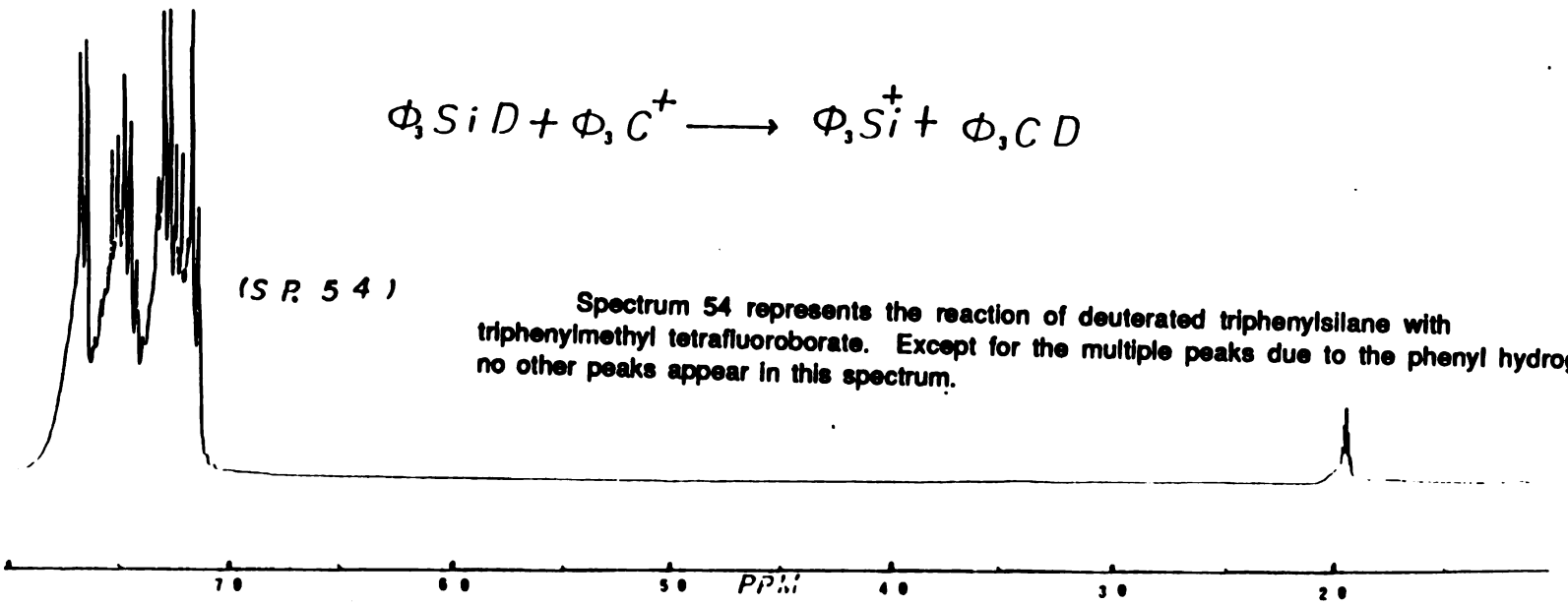
Spectrum 51 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of triphenylmethyl tetrafluoroborate. The peak of the silane hydrogen of the triphenylsilane appears at 5.48 ppm and that of the methine of triphenylmethane at 5.59 ppm.



Spectrum 52 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of anisyldiphenylmethyl tetrafluoroborate. The peak of the methine hydrogen of the anisyldiphenylmethane appears at 5.53 ppm.



Spectrum 53 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of trianisylmethyl tetrafluoroborate. The peak of the methine hydrogen of the trianisylmethane appears at 5.37 ppm.



Spectrum 54 represents the reaction of deuterated triphenylsilane with triphenylmethyl tetrafluoroborate. Except for the multiple peaks due to the phenyl hydrogens no other peaks appear in this spectrum.

Spectrum 51 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of triphenylmethyl tetrafluoroborate. The peak of the silane hydrogen of the triphenylsilane appears at 5.48 ppm and that of the methine of triphenylmethane at 5.59 ppm.

Spectrum 52 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of anisyldiphenylmethyl tetrafluoroborate. The peak of the methine hydrogen of the anisyldiphenylmethane appears at 5.53 ppm.

Spectrum 53 represents the reaction of equimolar amounts of triphenylsilane and its deuterated analog with an equimolar amount of trianisylmethyl tetrafluoroborate. The peak of the methine hydrogen of the trianisylmethane appears at 5.37 ppm.

Spectrum 54 represents the reaction of deuterated triphenylsilane with triphenylmethyl tetrafluoroborate. Except for the multiple peaks due to the phenyl hydrogens no other peaks appear in this spectrum.

RESULTS AND DISCUSSION

Calculations of rate constants and kinetic isotope effects ($^{k}H/^{k}D$).

Typically, these reactions involved the addition of equimolar amounts of triphenylsilane and its silyldeuterated counterpart to an equimolar amount of the cation, in deuteroacetonitrile solution. The reactions were generally exothermic and proceeded instantaneously, except for the reaction with the trianisylmethyl tetrafluoroborate (3), which proceeded at a much slower rate.

When two isotopic molecules, A_1 and A_2, undergo analogous irreversible reactions in intermolecular competition

$$A_1 + B \xrightarrow{k_1} (products)_1$$
$$A_2 + B \xrightarrow{k_2} (products)_2$$

the isotope effect is given by:

$$\frac{k_1}{k_2} = \frac{\log \frac{a_1}{a_1^\circ}}{\log \frac{a_2}{a_2^\circ}}$$

where a_1° and a_2° are the initial concentrations and a_1 and a_2 are the remaining fractions of the two isotopic species.

From the ^1H NMR spectra of the reaction mixture, the isotope effect was calculated by comparing the concentration of the triphenylsilane with that of the triphenylmethane (or anisyldiphenylmethane), which is equal to the concentration of unreacted deuterated triphenylsilane.

$$\frac{kH}{kD} = \frac{\log \frac{[A]}{[A_\circ]}}{\log \frac{[A_\circ - A]}{[A_\circ]}}$$

[A] = the area at 5.48 ppm of the triphenylsilane proton

[A∘] = the area of the triphenylsilane proton at 5.48 ppm plus the area of triphenylmethane methine proton at 5.59 ppm (or anisyldiphenylmethane methine proton at 5.53 ppm, or trianisylmethane methine proton at 5.37 ppm).

The isotope effect of reaction 3 was calculated from determination of the individual ^{k}H and ^{k}D, by following the procedure described for the reactions in Chapter II.

Triphenylmethyl cation reactions (1)[19]:

The reactions of triphenylmethyl tetrafluoroborate (sp. 51) with the triphenylsilanes were carried out twice. In the first run, an equimolar amount of triphenylsilane and its deuterated derivative dissolved in CD_3CN was added to an equimolar amount of solid triphenylmethyl tetrafluoroborate. The calculated $^{k}H/^{k}D$ was found to be 1.8±0.4. In the second run, an equimolar amount of the silane compounds dissolved in dideuteroacetonitrile, was added to an equimolar amount of triphenylmethyl tetrafluoroborate dissolved in CD_3CN; the isotope effect was calculated to be1.8±0.1. So, for this reaction $^{k}H/^{k}D$ = 1.8±0.4.

The reaction was also performed at -20°C. The isotope effect was found to be 2.1±03.

Anisyldiphenylmethyl cation reactions (2):

The reactions of anisyldiphenylmethyl tetrafluoroborate with the triphenylsilanes (sp. 52) were performed twice. In the first experiment equimolar amounts of each component dissolved in CD_3CN were added to solid anisyldiphenylmethyl tetrafluoroborate, giving an isotope effect of 2.03.

In the second experiment equimolar amounts of each silane compound dissolved in acetonitrile were added to an equimolar amount of anisyldiphenylmethyl tetrafluoroborate dissolved in acetonitrile, giving an isotope effect of 2.41.

So, the averaged $^{k}H/^{k}D = 2.2 \pm 0.2$ for this reaction.

Trianisylmethyl cation reactions (3):

The reaction of trianisylmethyl tetrafluoroborate with triphenylsilanes at 24°C is quite slow. For this reaction equimolar amounts of triphenylsilane and its silyl deuterated derivative dissolved in CD_3CN were reacted with an equimolar amount of the trianisylmethyl tetrafluoroborate. Upon completion of the reaction, as monitored by the disappearance of the methoxy proton peaks of the cation, 54-57% of the triphenylsilane (sp. 53) had reacted resulting in an isotope effect $^{k}H/^{k}D = 1.38 \pm 0.09$.

In a different experiment equimolar amounts of triphenylsilane and trianisylmethyl tetrafluoroborate were mixed together in acetonitrile at 25°C and the progress of the reaction was followed by NMR. After 77 minutes, 36.3% of the cation had reacted. From the integrated areas under the methoxy peaks for the reactant and product, by using the program which appers in the appendix, pages 94-95, the ^{k}H for the reaction was found to be $(2.00 \pm 0.03)\times10^{-3}$ (appendix, page 122). Similarly, for the deuterated triphenylsilane ^{k}D was found to be $(1.21 \pm 0.01)\times10^{-3}$ (appendix, page 123). In this reaction 26% of the cation had reacted in 79 minutes.

So, from this experiment $^{k}H/^{k}D = 1.66 \pm 0.03$ (appendix, page 142). A source of error in the reaction rates is due to the propionic anhydride trapped in the cation crystals during the cation preparation.

Search for possible hydride attack on carbons other than C-1 of the cations:

The NMR of the reaction of the triphenylmethyl cation with deuterated triphenylsilane (sp. 54) shows no proton peak in the region 5-6 ppm indicating that only deuterium has been transferred to the C-1 of the triphenylmethyl cation.

When the reaction of deuterated triphenylsilane reacted with 38.7% of the trianisylmethyl cation (3) the NMR spectrum showed no proton peak in the region of 5-6 ppm. This finding clearly demonstrates that the deuterium has been transferred from triphenylsilane to the central carbon of the trianisylmethyl cation.

Summary of the isotope effects for the reactions in this section

$$\phi_3SiH + \phi_3SiD + \phi_3C^+ \xrightarrow{24^\circ C} \phi_3Si^+ + \phi_3CH(D)$$

$$\frac{k_H}{k_D} = 1.8 \pm 0.4$$

$$\phi_3SiH + \phi_3SiD + \phi_3C^+ \xrightarrow{-20^\circ C} \phi_3Si^+ + \phi_3CH(D)$$

$$\frac{k_H}{k_D} = 2.1 \pm 0.3$$

$$\phi_3SiH + \phi_3SiD + (CH_3OC_6H_4)(C_6H_5)_2C^+ \xrightarrow{24^\circ C} \phi_3Si^+ + (CH_3OC_6H_4)(C_6H_5)_2CH(D)$$

$$\frac{k_H}{k_D} = 2.2 \pm 0.2$$

$$\phi_3SiH(D) + (CH_3OC_6H_4)_3C^+ \xrightarrow{25^\circ C} \phi_3Si^+ + (CH_3OC_6H_4)_3CH(D)$$

$$\frac{k_H}{k_D} = 1.66 \pm 0.03$$

Conclusions

All the reactions studied in this section are one-step hydride transfer from the donor hydrocarbon to the acceptor carbocation.

Investigations of the triphenylmethyl and trianisylmethyl tetrafluoroborate reactions with the triphenylsilanes confirm that the only cationic reacting center in the triarylmethyl tetrafluoroborates under the conditions of this study is the central carbon. Hydride attack on the aryl rings of the triarylmethyl tetrafluoroborates followed by rearrangement to the methine carbon does not occur.

The isotope effects of the triphenylsilane reactions are very small. Their magnitude lay in the range which was assigned by O'Ferral to a very small angle (around 90°) between donor-hydrogen-acceptor, on the assumption that the force constants on either side of the hydrogen are the same. Since in the triphenylsilane reactions the force constants on either side of the hydrogen are not expected to be the same no conclusions can be made for the transition state in these reactions.

GENERAL CONCLUSIONS

GENERAL CONCLUSIONS

All the reactions studied in this study which involve triarylmethanes with triarylmethyl cations; xanthenes with xanthyl, triarylmethyl and dianisylmethyl cations; and triphenylsilanes with triarylmethyl cations represent one-step hydride transfer reactions. The transfer occurs from the donor to the acceptor molecule with no new carbon-carbon bonds or any other products being formed.

Investigations of the triphenylmethyl, anisyldiphenylmethyl and trianisylmethyl cation reactions confirm that the only cationic reacting center in these cations under the conditions of this study is the methine carbon. Hydride attack on the aryl rings of the above cations followed by hydrogen rearrangement to the methine carbon does not occur. Also investigations of the 9-xanthyl, 2,6-dimethoxy-9-xanthyl and dianisylmethyl cation reactions lead to similar conclusions.

The very large isotope effects exhibited by the reaction of triarylmethanes with triarylmethyl cations, which are slightly larger that the maximum kinetic isotope effect O'Ferral calculated for linearity, support a linear transition state for these reactions. The reactions of xanthenes with xanthyl, triarylmethyl and dianisylmethyl cations also proceed with large kinetic isotope effects, which place them in the range assigned by O'Ferral to cases where the angle between donor-hydrogen-acceptor is 120°-150°, on the assumption that the force constant on either side of the hydrogen is the same. It is also possible that the transition state is linear with unequal force constants on either side of the hydrogen. No assessment of the structure of the transition states of the reactions of triphenylsilanes with triarylmethyl cations can be made because the small kinetic isotope effects, in the range assigned by O'Ferral to cases where the angle between donor-hydrogen-acceptor is about 90°, may be due to large differences in the force constants on either side of the hydrogen bonds in the transition state.

The identity reaction between the triphenylmethyl cation and triphenylmethane is quite slow compared with the corresponding reaction of xanthene and the 9-xanthyl cation.

APPENDIX

Computer program for the calculations of the rate constants of reactions 1 and 2 from Chapter II, 3 from Chapter III and 3 from Chapter IV.

```
#include <stdio.h>
#include <math.h>

#define LINE 80

main()
{
  FILE *pr;
  char data_file[20];

  float   t[30];
  float a,V,A3[30],A4[30];          /* data */

  int n;                            /* data number  */

  double y[30];
  double SumT=0,SumT2=0,SumY=0,SumY2=0,SumYT=0,SSt,SSy,SSty,SSE,SlopeDev;
  char title[80];
  int i;
  double store;

  double k,b;                        /* estimated slope and intersept */

  double sqrt();

  /*                        Read  data                              */

  scanf("%s",data_file);
  pr=fopen(data_file,"r");
  fgets(title,LINE,pr);
  fscanf(pr,"%f",&a);
  fscanf(pr,"%f",&V);
  i=0;
  while(!feof(pr))
  {
    fscanf(pr,"%f",&t[i]);
    fscanf(pr,"%f",&A3[i]);
    fscanf(pr,"%f",&A4[i]);
    y[i]=A3[i]*V/(1000*a*A4[i]);
    i++;
  }

  n=i-1;
  for (i=0;i<n;i++)
  {
    SumT=SumT+t[i];
    SumT2=SumT2+t[i]*t[i];
    SumY=SumY+y[i];
    SumY2=SumY2+y[i]*y[i];
    SumYT=SumYT+y[i]*t[i];
  }
  SSty=SumYT-SumY*SumT/n;
  SSt=SumT2-SumT*SumT/n;
  SSy=SumY2-SumY*SumY/n;
  k=SSty/SSt;
  b=(SumY-SumT*k)/n;
  SSE=SSy-SSty*SSty/SSt;
  SlopeDev=sqrt(SSE/((n-2)*SSt));

  /*                    Print results                                */

  printf("\n         %s\n\n\n",title);
  printf("         a=%f\n",a);
  printf("         V=%.3f\n\n",V);
  for (i=0;i<n;i++)
  {
```

```
  printf("        t=%.0f   ,A3=%5.3f  ,A4=%5.3f\n",t[i],A3[i],A4[i]);

printf("\n\n\n         Estimated intercept                    : %e\n",b);
printf("        Estimated slope                         : %e\n",k);
printf("        Slope Deviation                         : %e\n",SlopeDev);
printf("        95 percentage,confindence slope interval : %e +- %e\n",
                                k,2.306*SlopeDev);
```

REACTION 1,CHAPTER II,HYDRIDE TRANSFER,AT 22 'C

a=0.000283
V=1.145

t=5593 ,A3=1.667 ,A4=25.078
t=8053 ,A3=1.967 ,A4=22.450
t=9073 ,A3=2.344 ,A4=24.699
t=10033 ,A3=2.090 ,A4=22.021
t=11773 ,A3=3.179 ,A4=22.951
t=12973 ,A3=3.988 ,A4=24.332
t=14473 ,A3=3.575 ,A4=22.169
t=15913 ,A3=4.024 ,A4=22.627
t=16753 ,A3=4.143 ,A4=21.133
t=17773 ,A3=4.194 ,A4=22.196

Estimated intercept : -1.186035e-02
Estimated slope : 4.632594e-05
Slope Deviation : 3.599475e-06
95 percentage,confindence slope interval : 4.632594e-05 +- 8.300390e-06

REACTION 1 ,CHAPTER II,DEUTERIUM TRANSFER,AT 22 'C

a=0.000514
V=1.260

t=7393 ,A3=0.383 ,A4=21.116
t=11053 ,A3=0.287 ,A4=11.291
t=14593 ,A3=0.353 ,A4=10.955
t=18193 ,A3=0.512 ,A4=11.090
t=19993 ,A3=0.999 ,A4=20.496
t=21373 ,A3=1.140 ,A4=21.902
t=24013 ,A3=1.189 ,A4=21.502
t=25513 ,A3=1.308 ,A4=21.981
t=27313 ,A3=1.315 ,A4=20.423
t=29293 ,A3=0.739 ,A4=10.823

Estimated intercept : 1.575580e-03
Estimated slope : 5.724208e-06
Slope Deviation : 1.979729e-07
95 percentage,confindence slope interval : 5.724208e-06 +- 4.565254e-07

REACTION 1 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C

a=0.000624
V=2.340

t=8233 ,A3=2.336 ,A4=16.751
t=10213 ,A3=2.649 ,A4=14.080
t=13213 ,A3=3.045 ,A4=12.367
t=15073 ,A3=4.488 ,A4=17.478
t=17173 ,A3=4.393 ,A4=14.743

Estimated intercept : 2.972275e-02
Estimated slope : 6.389963e-05
Slope Deviation : 5.682635e-06
95 percentage,confindence slope interval : 6.389963e-05 +- 1.310416e-05

REACTION 1 , CHAPTER II ,DEUTERIUM TRANSFER , AT 30 'C

a=0.001100
V=2.570

t=11473 ,A3=0.859 ,A4=19.803
t=13753 ,A3=1.047 ,A4=20.875
t=17653 ,A3=1.356 ,A4=20.560
t=21013 ,A3=1.514 ,A4=20.398
t=24493 ,A3=1.745 ,A4=20.353
t=27013 ,A3=2.005 ,A4=20.002
t=34873 ,A3=2.480 ,A4=19.075

Estimated intercept : -1.536876e-03
Estimated slope : 8.618130e-06
Slope Deviation : 3.044688e-07
95 percentage,confindence slope interval : 8.618130e-06 +- 7.021051e-07

REACTION 1 , CHAPTER II , HYDRIDE TRANSFER , AT 40 'C

a=0.000230
V=1.115

t=1453 ,A3=0.805 ,A4=17.045
t=3853 ,A3=2.090 ,A4=15.504
t=4573 ,A3=2.156 ,A4=14.799
t=6253 ,A3=3.110 ,A4=14.088
t=6973 ,A3=3.402 ,A4=13.920
t=7633 ,A3=3.462 ,A4=13.568
t=9493 ,A3=4.445 ,A4=13.578

Estimated intercept : -1.807618e-02
Estimated slope : 1.688801e-04
Slope Deviation : 5.108333e-06
95 percentage,confindence slope interval : 1.688801e-04 +- 1.177982e-05

REACTION 1 , CHAPTER II , DEUTERIUM TRANSFER , AT 40 'C

a=0.000440
V=1.220

t=2593 ,A3=0.312 ,A4=13.276
t=4873 ,A3=0.502 ,A4=12.306
t=6193 ,A3=0.605 ,A4=11.449
t=7573 ,A3=0.695 ,A4=10.952
t=9373 ,A3=0.903 ,A4=11.804
t=11173 ,A3=1.037 ,A4=11.694
t=12973 ,A3=1.245 ,A4=11.985
t=14773 ,A3=1.604 ,A4=12.130
t=16573 ,A3=1.683 ,A4=12.236
t=18373 ,A3=1.889 ,A4=11.240
t=20173 ,A3=2.019 ,A4=11.896
t=21973 ,A3=1.967 ,A4=10.388

Estimated intercept : -7.019879e-03
Estimated slope : 2.414899e-05
Slope Deviation : 7.042705e-07
95 percentage,confindence slope interval : 2.414899e-05 +- 1.624048e-06

REACTION 1 , CHAPTER II ,HYDRIDE TRANSFER , AT 22 'C , SECOND PERFORMANCE

a=0.000250
V=1.130

t=4116 ,A3=0.401 ,A4=13.033
t=7296 ,A3=1.556 ,A4=26.518
t=10536 ,A3=1.071 ,A4=12.031
t=11736 ,A3=2.387 ,A4=23.679
t=12276 ,A3=2.255 ,A4=23.361

Estimated intercept : -1.838315e-02
Estimated slope : 3.901803e-05
Slope Deviation : 2.599130e-06
95 percentage,confindence slope interval : 3.901803e-05 +- 5.993594e-06

REACTION 1 CHAPTER II , DEUTERIUM TRANSFER , AT 22 'C , SECOND PERFORMANCE

a=0.000603
V=1.270

t=7836	,A3=0.173	,A4=11.173
t=11856	,A3=0.303	,A4=12.458
t=14316	,A3=0.341	,A4=12.320
t=16296	,A3=0.402	,A4=12.199
t=18036	,A3=0.453	,A4=12.030
t=20136	,A3=0.512	,A4=11.928
t=20916	,A3=0.558	,A4=11.903
t=21936	,A3=0.591	,A4=11.747
t=23076	,A3=0.594	,A4=11.636
t=28836	,A3=0.997	,A4=13.630
t=30156	,A3=1.020	,A4=14.348
t=31416	,A3=1.117	,A4=14.354
t=32496	,A3=1.168	,A4=14.434
t=33276	,A3=1.195	,A4=14.277

Estimated intercept : -2.221676e-02
Estimated slope : 5.855576e-06
Slope Deviation : 1.703260e-07
95 percentage,confindence slope interval : 5.855576e-06 +- 3.927719e-07

REACTION 1 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C , SECOND PERFORMANCE

a=0.000284
V=1.145

t=4716 ,A3=1.481 ,A4=16.202
t=5736 ,A3=1.808 ,A4=15.939
t=6456 ,A3=1.003 ,A4=7.911
t=7716 ,A3=1.211 ,A4=7.795
t=9156 ,A3=1.365 ,A4=7.370
t=10416 ,A3=3.038 ,A4=14.765
t=11316 ,A3=3.188 ,A4=14.396
t=12576 ,A3=3.597 ,A4=14.335

Estimated intercept : -5.140396e-03
Estimated slope : 8.069487e-05
Slope Deviation : 1.316096e-06
95 percentage,confindence slope interval : 8.069487e-05 +- 3.034917e-06

REACTION 1,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C ,SECOND PERFORMANCE

a=0.000527
V=1.240

t=8784 ,A3=0.489 ,A4=14.988
t=10716 ,A3=0.639 ,A4=14.672
t=12684 ,A3=0.781 ,A4=14.513
t=16476 ,A3=1.015 ,A4=14.384
t=17616 ,A3=1.084 ,A4=14.042
t=18696 ,A3=1.045 ,A4=13.710
t=19776 ,A3=1.211 ,A4=13.857
t=21024 ,A3=1.237 ,A4=13.723
t=21684 ,A3=1.293 ,A4=13.396
t=23196 ,A3=1.384 ,A4=13.686

Estimated intercept : -1.708431e-02
Estimated slope : 1.105344e-05
Slope Deviation : 3.380876e-07
95 percentage,confindence slope interval : 1.105344e-05 +- 7.796301e-07

REACTION 1,CHAPTER II,HYDRIDE TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

a=0.000173
V=1.080

t=5676 ,A3=2.181 ,A4=18.501
t=5676 ,A3=2.403 ,A4=18.501
t=6936 ,A3=1.533 ,A4=9.941
t=6936 ,A3=1.557 ,A4=9.941
t=8016 ,A3=1.612 ,A4=9.505
t=8016 ,A3=1.766 ,A4=9.593
t=8976 ,A3=1.840 ,A4=9.001
t=8976 ,A3=1.840 ,A4=8.912
t=9936 ,A3=1.908 ,A4=8.418

Estimated intercept : -8.490976e-02
Estimated slope : 1.512577e-04
Slope Deviation : 8.242115e-06
95 percentage,confindence slope interval : 1.512577e-04 +- 1.900632e-05

REACTION 1 ,CHAPTER II ,DEUTARIUM TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

a=0.000485
V=1.255

t=5976 ,A3=0.479 ,A4=11.812
t=7476 ,A3=0.572 ,A4=11.308
t=9696 ,A3=0.784 ,A4=11.139
t=11136 ,A3=0.885 ,A4=10.840
t=12816 ,A3=1.025 ,A4=10.760
t=14196 ,A3=1.138 ,A4=10.556
t=15660 ,A3=1.239 ,A4=10.441
t=17256 ,A3=1.350 ,A4=10.353
t=18696 ,A3=1.477 ,A4=10.197
t=20196 ,A3=1.555 ,A4=10.088
t=21876 ,A3=1.677 ,A4=9.781

Estimated intercept : -2.452276e-02
Estimated slope : 2.120430e-05
Slope Deviation : 1.937635e-07
95 percentage,confindence slope interval : 2.120430e-05 +- 4.468187e-07

REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 25 'C

a=0.000645
V=1.315

t=334236 ,A3=1.420 ,A4=31.428
t=370536 ,A3=1.572 ,A4=30.308
t=535296 ,A3=1.985 ,A4=27.259
t=669936 ,A3=2.917 ,A4=30.658
t=774396 ,A3=3.290 ,A4=27.498
t=853476 ,A3=3.408 ,A4=28.124
t=1126656 ,A3=4.103 ,A4=27.051

Estimated intercept : 2.560769e-03
Estimated slope : 2.835421e-07
Slope Deviation : 1.734029e-08
95 percentage,confindence slope interval : 2.835421e-07 +- 3.998671e-08

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 25 'C

a=0.000659
V=1.305

t=528456 ,A3=0.237 ,A4=23.272
t=679416 ,A3=0.261 ,A4=29.717
t=1119756 ,A3=0.617 ,A4=28.235

Estimated intercept	: -6.813830e-03
Estimated slope	: 4.350970e-08
Slope Deviation	: 1.568575e-08
95 percentage,confindence slope interval	: 4.350970e-08 +- 3.617133e-08

REACTION 2 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C

a=0.000645
V=1.315

t=71256 ,A3=1.010 ,A4=48.690
t=99036 ,A3=0.729 ,A4=24.405
t=115716 ,A3=0.794 ,A4=25.974
t=145236 ,A3=0.917 ,A4=23.156
t=168336 ,A3=2.025 ,A4=41.178
t=228036 ,A3=1.445 ,A4=22.571
t=274416 ,A3=2.739 ,A4=31.838
t=331416 ,A3=3.492 ,A4=35.859
t=362556 ,A3=3.790 ,A4=38.024
t=413436 ,A3=2.676 ,A4=22.566
t=495336 ,A3=6.980 ,A4=46.460
t=576516 ,A3=4.645 ,A4=28.849
t=610896 ,A3=4.519 ,A4=26.374
t=611916 ,A3=4.341 ,A4=26.581

Estimated intercept : 4.288991e-03
Estimated slope : 5.667576e-07
Slope Deviation : 1.443641e-08
95 percentage,confindence slope interval : 5.667576e-07 +- 3.329035e-08

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C

a=0.000659
V=1.305

t=356016 ,A3=0.274 ,A4=23.021
t=524736 ,A3=0.472 ,A4=27.764
t=523476 ,A3=0.478 ,A4=28.464
t=517416 ,A3=0.569 ,A4=31.528
t=607356 ,A3=0.469 ,A4=26.546
t=675276 ,A3=0.636 ,A4=29.499
t=761856 ,A3=0.605 ,A4=26.120
t=841056 ,A3=0.715 ,A4=26.432
t=919356 ,A3=0.887 ,A4=26.919
t=1010136 ,A3=0.839 ,A4=21.506
t=1111956 ,A3=0.983 ,A4=28.372
t=1115436 ,A3=1.025 ,A4=29.144

Estimated intercept : -1.763872e-03
Estimated slope : 6.752233e-08
Slope Deviation : 5.620164e-09
95 percentage,confindence slope interval : 6.752233e-08 +- 1.296010e-08

REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C

a=0.000645
V=1.315

t=75096 ,A3=1.417 ,A4=28.902
t=119496 ,A3=2.109 ,A4=26.965
t=143436 ,A3=2.160 ,A4=20.795
t=169956 ,A3=4.360 ,A4=37.072
t=229956 ,A3=3.796 ,A4=21.792
t=289716 ,A3=6.920 ,A4=33.000

Estimated intercept : -2.002436e-02
Estimated slope : 1.570332e-06
Slope Deviation : 5.872941e-08
95 percentage,confindence slope interval : 1.570332e-06 +- 1.354300e-07

REACTION 2 ,CHAPTER II,DEUTERIUN TRANSFER ,AT 40 'C

a=0.000659
V=1.305

t=113136 ,A3=0.240 ,A4=25586.000
t=273876 ,A3=1.029 ,A4=41.931
t=274776 ,A3=0.420 ,A4=18.798
t=324696 ,A3=1.229 ,A4=46.139
t=357996 ,A3=1.323 ,A4=43.190
t=488916 ,A3=1.076 ,A4=23.435
t=521616 ,A3=1.440 ,A4=29.997
t=571956 ,A3=1.106 ,A4=26.480
t=605376 ,A3=1.655 ,A4=31.836
t=676896 ,A3=1.520 ,A4=28.362
t=764376 ,A3=1.756 ,A4=27.528
t=843036 ,A3=1.703 ,A4=24.224
t=921996 ,A3=3.730 ,A4=43.000
t=1011756 ,A3=4.160 ,A4=45.980
t=1116996 ,A3=2.535 ,A4=27.777

Estimated intercept : -6.441041e-03
Estimated slope : 1.779391e-07
Slope Deviation : 8.073938e-09
95 percentage,confindence slope interval : 1.779391e-07 +- 1.861850e-08

REACTION 2 , CHAPTER II , HYDRIDE TRANSFER , AT 25 'C , SECOND PERFORMANCE

a=0.000614
V=1.250

t=187236 ,A3=0.745 ,A4=30.663
t=269376 ,A3=1.332 ,A4=31.646
t=385596 ,A3=1.914 ,A4=31.252
t=504936 ,A3=2.367 ,A4=31.697
t=715356 ,A3=3.421 ,A4=31.501

Estimated intercept : -3.350863e-03
Estimated slope : 3.150097e-07
Slope Deviation : 1.479111e-08
95 percentage,confindence slope interval : 3.150097e-07 +- 3.410829e-08

REACTION 2 ,CHAPTER II,DEUTERIUM TRANSFER ,AT 25 'C ,SECOND PERFORMANCE

a=0.000638
V=1.320

t=331896 ,A3=0.176 ,A4=33.952
t=448356 ,A3=0.293 ,A4=35.231
t=567996 ,A3=0.193 ,A4=17.560
t=778116 ,A3=0.276 ,A4=18.465

Estimated intercept : -3.410016e-03
Estimated slope : 4.478856e-08
Slope Deviation : 2.701426e-09
95 percentage,confindence slope interval : 4.478856e-08 +- 6.229488e-09

REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 30 'C ,SECOND PERFORMANCE

a=0.000614
V=1.250

t=173316 ,A3=1.539 ,A4=30.562
t=192356 ,A3=1.756 ,A4=30.217
t=263796 ,A3=2.100 ,A4=28.661
t=376416 ,A3=2.524 ,A4=24.785
t=391356 ,A3=3.442 ,A4=29.814
t=502776 ,A3=3.756 ,A4=27.649
t=701796 ,A3=5.366 ,A4=28.359

Estimated intercept : 1.319959e-02
Estimated slope : 5.310615e-07
Slope Deviation : 1.623446e-08
95 percentage,confindence slope interval : 5.310615e-07 +- 3.743667e-08

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C ,SECOND PERFORMANCE

a=0.000638
V=1.320

t=246036 ,A3=0.152 ,A4=15.966
t=327216 ,A3=0.305 ,A4=30.602
t=439116 ,A3=0.355 ,A4=27.931
t=450876 ,A3=0.572 ,A4=33.043
t=557976 ,A3=0.327 ,A4=16.304
t=772056 ,A3=0.637 ,A4=27.199

Estimated intercept : 4.001516e-03
Estimated slope : 6.027745e-08
Slope Deviation : 1.001937e-08
95 percentage,confindence slope interval : 6.027745e-08 +- 2.310467e-08

REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

a=0.000614
V=1.250

t=84336 ,A3=1.394 ,A4=28.109
t=85896 ,A3=1.474 ,A4=28.818
t=107796 ,A3=1.556 ,A4=24.747
t=109056 ,A3=1.761 ,A4=24.892
t=171516 ,A3=2.768 ,A4=26.840
t=200856 ,A3=3.556 ,A4=27.484
t=244596 ,A3=4.031 ,A4=25.411
t=266676 ,A3=4.872 ,A4=26.893

Estimated intercept : -2.037524e-02
Estimated slope : 1.420612e-06
Slope Deviation : 4.385447e-08
95 percentage,confindence slope interval : 1.420612e-06 +- 1.011284e-07

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

a=0.000638
V=1.320

t=159156 ,A3=0.382 ,A4=28.961
t=243816 ,A3=0.349 ,A4=16.946
t=328716 ,A3=0.456 ,A4=16.452
t=442356 ,A3=0.540 ,A4=14.948
t=560076 ,A3=1.289 ,A4=30.688
t=561636 ,A3=1.240 ,A4=28.756

Estimated intercept : 5.983360e-03
Estimated slope : 1.490609e-07
Slope Deviation : 6.869764e-09
95 percentage,confindence slope interval : 1.490609e-07 +- 1.584168e-08

REACTION 3 , CHAPTER III , HYDRIDE TRANSFER , AT 25 'C

a=0.000140
V=2.020

t=1815 ,A3=5.132 ,A4=10.963
t=3015 ,A3=7.434 ,A4=9.327
t=4815 ,A3=9.789 ,A4=7.647
t=7635 ,A3=11.859 ,A4=5.533

Estimated intercept : -1.014366e+00
Estimated slope : 4.144135e-03
Slope Deviation : 9.775526e-05
95 percentage,confindence slope interval : 4.144135e-03 +- 2.254236e-04

REACTION 3 , CHAPTER III , DEUTERIUM TRANSFER , AT 25 'C

a=0.000140
V=2.020

t=1515 ,A3=0.536 ,A4=7.271
t=3015 ,A3=1.960 ,A4=13.200
t=4875 ,A3=2.842 ,A4=12.585
t=6435 ,A3=3.579 ,A4=12.267
t=8295 ,A3=4.351 ,A4=11.290
t=10335 ,A3=4.999 ,A4=10.679
t=12255 ,A3=5.720 ,A4=10.196

Estimated intercept : 1.102714e-01
Estimated slope : 6.477706e-04
Slope Deviation : 6.987873e-06
95 percentage,confindence slope interval : 6.477706e-04 +- 1.611404e-05

REACTION 3 , CHAPTER IV , HYDRIDE TRANSFER , AT 25 'C

a=0.000389
V=6.180

t=1455 ,A3=2.862 ,A4=15.635
t=2595 ,A3=4.258 ,A4=13.320
t=3735 ,A3=5.658 ,A4=12.254
t=4635 ,A3=6.550 ,A4=11.494
t=6375 ,A3=8.257 ,A4=10.261

Estimated intercept : -9.578710e-02
Estimated slope : 2.002580e-03
Slope Deviation : 3.112737e-05
95 percentage,confindence slope interval : 2.002580e-03 +- 7.177971e-05

REACTION 3 ,CHAPTER IV ,DEUTERIUM TRANSFER , AT 25 'C

a=0.000389
V=6.180

t=3015 ,A3=3.569 ,A4=16.601
t=4755 ,A3=5.511 ,A4=15.691
t=7395 ,A3=6.883 ,A4=12.464
t=8535 ,A3=3.596 ,A4=5.679

Estimated intercept : -1.885836e-01
Estimated slope : 1.206016e-03
Slope Deviation : 1.270632e-05
95 percentage,confindence slope interval : 1.206016e-03 +- 2.930077e-05

Computer program for the calculations of the rate constants of reaction 3 from Chapter II.

```
#include <stdio.h>
#include <math.h>

#define LINE 80

main()
{
  FILE *pr;
  char data_file[20];

  float   t[30];
  float a,V,A3[30],A4[30];          /* data */

  int n;                            /* data number  */

  double y[30];
  double SumT=0,SumT2=0,SumY=0,SumY2=0,SumYT=0,SSt,SSy,SSty,SSE,SlopeDev;
  char title[80];
  int i;
  double store;

  double k,b;                        /* estimated slope and intersept */

  double sqrt();

  /*                        Read  data                          */

  scanf("%s",data_file);
  pr=fopen(data_file,"r");
  fgets(title,LINE,pr);
  fscanf(pr,"%f",&a);
  fscanf(pr,"%f",&V);
  i=0;
  while(!feof(pr))
  {
    fscanf(pr,"%f",&t[i]);
    fscanf(pr,"%f",&A3[i]);
    fscanf(pr,"%f",&A4[i]);
    y[i]=A4[i]*V/(3000*a*A3[i]);
    i++;
  }

  n=i-1;
  for (i=0;i<n;i++)
  {
    SumT=SumT+t[i];
    SumT2=SumT2+t[i]*t[i];
    SumY=SumY+y[i];
    SumY2=SumY2+y[i]*y[i];
    SumYT=SumYT+y[i]*t[i];
  }
  SSty=SumYT-SumY*SumT/n;
  SSt=SumT2-SumT*SumT/n;
  SSy=SumY2-SumY*SumY/n;
  k=SSty/SSt;
  b=(SumY-SumT*k)/n;
  SSE=SSy-SSty*SSty/SSt;
  SlopeDev=sqrt(SSE/((n-2)*SSt));

  /*                   Print results                                */

  printf("\n         %s\n\n\n",title);
  printf("        a=%f\n",a);
  printf("        V=%.3f\n\n",V);
  for (i=0;i<n;i++)
  {
```

```
  printf("        t=%.0f   ,A3=%5.3f  ,A4=%5.3f\n",t[i],A3[i],A4[i]);
 }
 printf("\n\n\n         Estimated intercept                    : %e\n",b);
 printf("        Estimated slope                         : %e\n",k);
 printf("        Slope Deviation                         : %e\n",SlopeDev);
 printf("        95 percentage,confindence slope interval : %e +- %e\n",
                              k,2.306*SlopeDev);
}
```

REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 26 'C

a=0.000523
V=1.260

t=212616 ,A3=4.106 ,A4=0.523
t=317556 ,A3=3.299 ,A4=0.662
t=408756 ,A3=4.263 ,A4=1.022
t=575280 ,A3=4.021 ,A4=1.424
t=809436 ,A3=3.563 ,A4=1.732
t=908556 ,A3=3.247 ,A4=1.861

Estimated intercept : -4.947268e-03
Estimated slope : 5.018885e-07
Slope Deviation : 1.419884e-08
95 percentage,confindence slope interval : 5.018885e-07 +- 3.274253e-08

REACTION 3,CHAPTER II ,DEUTERIUM TRANSFER ,AT 26 'C

a=0.000536
V=1.250

t=570996 ,A3=4.608 ,A4=0.151
t=805296 ,A3=4.099 ,A4=0.195
t=904116 ,A3=3.117 ,A4=0.213
t=1076316 ,A3=4.763 ,A4=0.359
t=1411356 ,A3=4.440 ,A4=0.422

Estimated intercept : -6.213155e-03
Estimated slope : 5.853886e-08
Slope Deviation : 7.640961e-09
95 percentage,confindence slope interval : 5.853886e-08 +- 1.762006e-08

REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 30 'C

a=0.000523
V=1.260

t=109596 ,A3=5.797 ,A4=0.771
t=282996 ,A3=3.346 ,A4=1.024
t=404856 ,A3=2.770 ,A4=1.218
t=484056 ,A3=2.930 ,A4=1.538
t=572796 ,A3=4.536 ,A4=2.812
t=664116 ,A3=5.854 ,A4=4.349
t=918156 ,A3=3.087 ,A4=3.224

Estimated intercept : -8.735520e-03
Estimated slope : 9.091740e-07
Slope Deviation : 1.913343e-08
95 percentage,confindence slope interval : 9.091740e-07 +- 4.412170e-08

REACTION 3,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C

a=0.000536
V=1.250

t=400236 ,A3=2.415 ,A4=0.114
t=564900 ,A3=4.721 ,A4=0.333
t=730836 ,A3=2.359 ,A4=0.204
t=909696 ,A3=4.553 ,A4=0.522

Estimated intercept : -3.342863e-03
Estimated slope : 1.002613e-07
Slope Deviation : 6.269703e-09
95 percentage,confindence slope interval : 1.002613e-07 +- 1.445793e-08

REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C

a=0.000523
V=1.260

t=41376 ,A3=8.144 ,A4=1.040
t=63756 ,A3=3.273 ,A4=0.447
t=107016 ,A3=4.250 ,A4=1.040
t=138816 ,A3=2.709 ,A4=0.832
t=208536 ,A3=3.680 ,A4=1.868
t=281436 ,A3=3.191 ,A4=2.335
t=397656 ,A3=2.690 ,A4=3.097
t=660096 ,A3=4.149 ,A4=7.692
t=904956 ,A3=3.458 ,A4=9.829

Estimated intercept : -7.785384e-02
Estimated slope : 2.515801e-06
Slope Deviation : 7.352940e-08
95 percentage,confindence slope interval : 2.515801e-06 +- 1.695588e-07

REACTION 3 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 40 'C

a=0.000536
V=1.250

t=130416 ,A3=5.771 ,A4=0.183
t=208716 ,A3=3.572 ,A4=0.198
t=273756 ,A3=3.210 ,A4=0.228
t=393696 ,A3=4.441 ,A4=0.566
t=473796 ,A3=4.371 ,A4=0.687
t=652236 ,A3=3.571 ,A4=0.756
t=734016 ,A3=3.106 ,A4=0.753
t=900696 ,A3=4.132 ,A4=1.285

Estimated intercept : -1.527714e-02
Estimated slope : 2.816871e-07
Slope Deviation : 6.152088e-09
95 percentage,confindence slope interval : 2.816871e-07 +- 1.418671e-08

REACTION 3 , CHAPTER II , HYDRIDE TRANSFER , AT 26 'C , SECOND PERFORMANCE

a=0.000578
V=1.285

t=102156 ,A3=3.956 ,A4=0.206
t=269136 ,A3=4.081 ,A4=0.620
t=342516 ,A3=3.457 ,A4=0.685
t=554616 ,A3=3.336 ,A4=1.092

Estimated intercept : -7.993816e-03
Estimated slope : 4.514002e-07
Slope Deviation : 2.328562e-09
95 percentage,confindence slope interval : 4.514002e-07 +- 5.369663e-09

REACTION 3 , CHAPTER II , DEUTERIUM TRANSFER , AT 26 'C , SECOND PERFORMANCE

a=0.000618
V=1.280

t=328896 ,A3=2.725 ,A4=0.049
t=613296 ,A3=4.242 ,A4=0.130
t=661776 ,A3=2.375 ,A4=0.087
t=860556 ,A3=4.696 ,A4=0.210
t=1255956 ,A3=4.434 ,A4=0.293
t=1520952 ,A3=2.642 ,A4=0.255
t=1449372 ,A3=4.848 ,A4=0.413

Estimated intercept : -4.477824e-03
Estimated slope : 4.368394e-08
Slope Deviation : 3.037173e-09
95 percentage,confindence slope interval : 4.368394e-08 +- 7.003721e-09

REACTION 3 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C , SECOND PERFORMANCE

a=0.000578
V=1.285

t=99996 ,A3=3.647 ,A4=0.336
t=189216 ,A3=3.459 ,A4=0.640
t=265056 ,A3=4.044 ,A4=1.157
t=339096 ,A3=3.018 ,A4=1.061
t=550476 ,A3=2.997 ,A4=1.913

Estimated intercept : -2.950594e-02
Estimated slope : 8.993287e-07
Slope Deviation : 3.213138e-08
95 percentage,confindence slope interval : 8.993287e-07 +- 7.409497e-08

REACTION 3 , CHAPTER II , DEUTERIUM TRANSFER , AT 30 'C , SECOND PERFORMANCE

a=0.000618
V=1.280

t=323916 ,A3=4.944 ,A4=0.169
t=608856 ,A3=4.304 ,A4=0.303
t=659676 ,A3=2.188 ,A4=0.165
t=842436 ,A3=4.805 ,A4=0.480
t=1001856 ,A3=4.285 ,A4=0.451
t=1284576 ,A3=3.856 ,A4=0.518

Estimated intercept : 4.323380e-03
Estimated slope : 7.050581e-08
Slope Deviation : 4.890307e-09
95 percentage,confindence slope interval : 7.050581e-08 +- 1.127705e-08

REACTION 3 , CHAPTER II , HYDRIDE TRANSFER , AT 40 'C , SECOND PERFORMANCE

a=0.000578
V=1.285

t=96456 ,A3=3.035 ,A4=0.859
t=165756 ,A3=5.781 ,A4=2.914
t=187056 ,A3=6.063 ,A4=3.512
t=251856 ,A3=3.170 ,A4=2.415
t=270816 ,A3=2.859 ,A4=2.440
t=558456 ,A3=4.404 ,A4=8.016

Estimated intercept : -3.752382e-02
Estimated slope : 2.472306e-06
Slope Deviation : 3.257347e-08
95 percentage,confindence slope interval : 2.472306e-06 +- 7.511442e-08

REACTION 3 , CHAPTER II , DEUTERIUM TRANSFER , AT 40 'C , SECOND PERFORMANCE

a=0.000618
V=1.280

t=154776 ,A3=4.018 ,A4=0.189
t=318936 ,A3=4.035 ,A4=0.424
t=397476 ,A3=3.764 ,A4=0.479
t=604776 ,A3=3.817 ,A4=0.854
t=657696 ,A3=3.804 ,A4=0.925
t=823536 ,A3=3.844 ,A4=1.178
t=1003896 ,A3=4.468 ,A4=1.693

Estimated intercept : -1.406858e-02
Estimated slope : 2.745121e-07
Slope Deviation : 5.424760e-09
95 percentage,confindence slope interval : 2.745121e-07 +- 1.250950e-08

Kinetic isotope effects of reaction 1 from Chapter II.

REACTION 1 ,CHAPTER II,DEUTERIUM TRANSFER,AT 22 'C
REACTION 1, CHAPTER II,HYDRIDE TRANSFER,AT 22 'C

kH/kD interval :8.092986 +- 0.688297

REACTION 1 , CHAPTER II ,DEUTERIUM TRANSFER , AT 30 'C
REACTION 1 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C

kH/kD interval :7.414559 +- 0.709507

REACTION 1 , CHAPTER II , DEUTERIUM TRANSFER , AT 40 'C
REACTION 1 , CHAPTER II , HYDRIDE TRANSFER , AT 40 'C

kH/kD interval :6.993256 +- 0.293839

REACTION 1,CHAPTER II ,DEUTERIUM TRANSFER , AT 22 'C ,SECOND PERFORMANCE
REACTION 1 ,CHAPTER II ,HYDRIDE TRANSFER , AT 22 'C , SECOND PERFORMANCE

kH/kD interval :6.663398 +- 0.484346

REACTION 1,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C ,SECOND PERFORMANCE
REACTION 1 ,CHAPTER II ,HYDRIDE TRANSFER , AT 30 'C , SECOND PERFORMANCE

kH/kD interval :7.300432 +- 0.253057

REACTION 1 ,CHAPTER II ,DEUTARIUM TRANSFER ,AT 40 'C ,SECOND PERFORMANCE
REACTION 1,CHAPTER II,HYDRIDE TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

kH/kD interval :7.133349 +- 0.394128

Kinetic isotope effects of reaction 2 from Chapter II.

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 25 'C
REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 25 'C

kH/kD interval :6.516756 +- 2.382929

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C
REACTION 2 , CHAPTER II , HYDRIDE TRANSFER , AT 30 'C

kH/kD interval :8.393631 +- 0.730619

REACTION 2 ,CHAPTER II,DEUTERIUN TRANSFER ,AT 40 'C
REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C

kH/kD interval :8.825111 +- 0.518927

REACTION 2 ,CHAPTER II,DEUTERIUM TRANSFER ,AT 25 'C ,SECOND PERFORMANCE
REACTION 2 , CHAPTER II ,HYDRIDE TRANSFER ,AT 25 'C , SECOND PERFORMANCE

kH/kD interval :7.033263 +- 0.537602

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C ,SECOND PERFORMANCE
REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 30 'C ,SECOND PERFORMANCE

kH/kD interval :8.810286 +- 1.489014

REACTION 2 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 40 'C ,SECOND PERFORMANCE
REACTION 2 ,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C ,SECOND PERFORMANCE

kH/kD interval :9.530413 +- 0.528656

Kinetic isotope effects of reaction 3 from Chapter II.

REACTION 3,CHAPTER II ,DEUTERIUM TRANSFER ,AT 26 'C
REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 26 'C

kH/kD interval :8.573595 +- 1.145079

REACTION 3,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C
REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 30 'C

kH/kD interval :9.068047 +- 0.598308

REACTION 3 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 40 'C
REACTION 3,CHAPTER II ,HYDRIDE TRANSFER ,AT 40 'C

kH/kD interval :8.931192 +- 0.325861

REACTION 3 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 26 'C ,SECOND PERFORMANCE
REACTION 3 , CHAPTER II ,HYDRIDE TRANSFER , AT 26 'C ,SECOND PERFORMANCE

kH/kD interval :10.333322 +- 0.720410

REACTION 3 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 30 'C ,SECOND PERFORMANCE
REACTION 3 ,CHAPTER II ,HYDRIDE TRANSFER , AT 30 'C , SECOND PERFORMANCE

kH/kD interval :12.755385 +- 0.995195

REACTION 3 ,CHAPTER II ,DEUTERIUM TRANSFER ,AT 40 'C ,SECOND PERFORMANCE
REACTION 3 ,CHAPTER II ,HYDRIDE TRANSFER , AT 40 'C , SECOND PERFORMANCE

kH/kD interval :9.006182 +- 0.213905

Kinetic isotope effect of reaction 3 from Chapter III.

REACTION 3 , CHAPTER III , DEUTERIUM TRANSFER , AT 25 'C
REACTION 3 , CHAPTER III , HYDRIDE TRANSFER , AT 25 'C

kH/kD interval :6.397535 +- 0.165942

Kinetic isotope effect of reaction 3 from Chapter IV.

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REACTION 3 ,CHAPTER IV ,DEUTERIUM TRANSFER , AT 25 'C
REACTION 3 , CHAPTER IV , HYDRIDE TRANSFER , AT 25 'C

   kH/kD interval :1.660492 +- 0.031181
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REFERENCES

REFERENCES

1. Westheimer, F.H. Chem. Rev. **1961**, 61, 265.

2. Melander, L. "Isotope effects on Reaction Rates," Ronald, New York, 1960, p. 24.

3. Hawthorne, M.F. and Lewis, E.S. J. Am. Chem. Soc. **1958**, 4296.

4. a.) Olah, G.A., DeMember, T.R. and Shen, J. J. Am. Chem. Soc. **1973**, 95, 4952.
   b.) Olah, G.A., Mo, Y.K. and Olah, J.A. J. Am. Chem. Soc. **1973**, 95, 4939.
   c.) Olah, G.A., Halpern, Y., Shen, J. and Mo, Y.K. J. Am. Chem. Soc. **1971**, 93, 1251.
   d.) Olah, G.A. and Svoboda, J.J. J. Am. Chem. Soc. **1973**, 95, 3794.

5. Raghavachari, K., Whiteside, R.A., Pople, J.A. and Schleyer, P.V.R. J. Am. Chem. Soc. **1981**, 103, 5649.

6. Saunders, M., Vogel, P., Hagen, E.L. and Rosenfield J. Acc. Chem. Res. **1973**, 6, 53.

7. Hariharon, P.C., Radoni, L., Pople, J.A. and Schleyer, P.V.R. J. Am. Chem. Soc. **1974**, 96, 599.

8. Kirchen, R.P. and Sorensen, T.S. J. Chem. Soc., Chem. Comm. **1978**, 769.

9. O'Ferrall, R.A.M. J. Chem. Soc. **1970**, B, 785.

10. Bartlett, P.D. and McCollum, J.D. J. Am. Chem. Soc. **1956**, 78, 1441.

11. Ray, G.J., Kurland, S.J. and Colter, A. Tetrahedron **1971**, 27, 735.

12. Bachmann, W.E. and Hetzner, H.P. Organic Syntheses, Collective volume 3, 841.

13. Deno, C., Jaruzelski, J.J. and Schriesheim, A. J. Am. Chem. Soc. (1955), 77, 3044.

14. Newman, M.S. and Deno, N.C. J. Am. Chem. Soc. **1951**, 73, 3644.

15. Dauben, H.J., Lewis, H.R. and Kenneth, H.M. J. Org. Chem. **1960**, 25, 1442.

16. Grover, P.K., Shah, G.D. and Shah, R.C. J.C.S., Part IV, 3982, (1955).

17. Brook, A.G., Gilman, H. and Miller, L.S. J. Am. Chem. Soc. **1953**, 75, 4759.

18. Benkesser, K.H., Landesmar, H. and Foster, D.J. J. Am. Chem. Soc. **1952**, 74, 648.

19. Lambert, J.B., McConnell, J.A. and Schulz, W.J., Jr. J. Am. Chem. Soc **1986**, 108, 2482.