

RELATIVE CONTRIBUTIONS OF HYPERCONJUGATION AND
NONBONDED INTERACTIONS TO SECONDARY
ISOTOPE EFFECTS

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1967



This is to certify that the

thesis entitled

RELATIVE CONTRIBUTIONS OF HYPERCONJUGATION AND
NONBONDED INTERACTIONS TO SECONDARY ISOTOPE EFFECTS

presented by

George Carl Sonnichsen

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry

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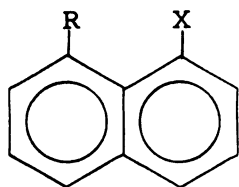
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ABSTRACT

RELATIVE CONTRIBUTIONS OF HYPERCONJUGATION AND NONBONDED INTERACTIONS TO SECONDARY ISOTOPE EFFECTS

by George Carl Sonnichsen

Secondary beta isotope effects in S_N1 reactions have generally been attributed to greater hyperconjugative stabilization of the carbonium ion like transition state by the protium compound. Bartell (1) has proposed that these isotope effects may be due to greater relief of non-bonded interactions for the hydrogen compound than the deuterium compound while proceeding from the reactant to the transition state. He also devised a method to calculate the isotope effects originating from non-bonded interactions. In order to ascertain the reliability of Bartell's method of calculation, the isotope effects were measured for the solvolysis of compounds I-III, i.e. systems where hyperconjugation is not possible, and these isotope effects were compared with the isotope effects calculated for these compounds.



Ia	R = D,	X = CH ₂ Cl
Ib	R = CD ₃ ,	X = CH ₂ Cl
Ic	R = CH ₃ ,	X = CD ₂ Cl
IIa	R = D,	X = COCl
IIb	R = CD ₃ ,	X = COCl
IIIa	R = D,	X = CO ₂ CH ₃
IIIb	R = CD ₃ ,	X = CO ₂ CH ₃

The isotope effect for solvolysis of 8-methyl-d₃-1-naphthylcarbinyl chloride (Ib) in 66.67% acetone-water (v/v) was found to be $k_H/k_D = 1.013 \pm 0.022$ at 25°. From kinetic measurements at 15° and 35° it was established that

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$\Delta H_H^\ddagger - \Delta H_D^\ddagger = 140 \pm 300$ cal/mole and $\Delta S_H^\ddagger - \Delta S_D^\ddagger = 0.49 \pm 0.44$ cal/deg/mole. The alpha isotope effect, $k_H/k_D = 1.32$, for the solvolysis of Ic indicates that the mechanism of the reaction is S_N1 . The isotope effect of Ia was determined by Scheppele (2) and the isotope effects of II and III by Papaioannou (3).

In most of these cases the calculated isotope effects agree with the experimental ones, thus indicating that Bartell's method can be used to predict the magnitude of isotope effects due to non-bonded interactions. However, the isotope effects which were calculated for systems where hyperconjugation is possible were not in accord with the experimental values. For t-butyl chloride- d_9 , acetyl chloride- d_3 and ethyl acetate- d_3 the calculated isotope effects were much less than the experimental ones. Thus it was concluded that in most systems, where hyperconjugation is possible, the major portion of the isotope effect is due to hyperconjugation.

REFERENCES

1. L. S. Bartell, J. Am. Chem. Soc., 83, 3567 (1961).
2. S. E. Scheppele, Ph.D. Thesis, Michigan State University, 1964.
3. C. G. Papaioannou, Ph.D. Thesis, Michigan State University, 1967.

RELATIVE CONTRIBUTIONS OF HYPERCONJUGATION AND
NONBONDED INTERACTIONS TO SECONDARY ISOTOPE EFFECTS

By

George Carl Sonnichsen

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1967

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INTRODUCTION

There are two main types of hydrogen isotope effects on a chemical reaction; primary effects, which involve forming or breaking of the isotopic bonds during the reaction, and secondary effects, where the bonds to the isotopic species are not broken in the course of the reaction. Secondary isotope effects can be classified either as effects where the isotopic species undergoes spatial reorientation during the reaction (α isotope effects) or effects where no spatial reorientation occurs (β, γ , etc. isotope effects).

To a close approximation secondary isotope effects arise from changes in force constants between the reactants and the transition state in a kinetic process, or between the reactants and the products in an equilibrium process (1). These force constant changes are manifested in vibrational frequency differences from which the isotope effects can be calculated (2). The physical organic chemist attempts to determine the origin of these force constant changes in terms of more descriptive terms such as inductive effects, hyperconjugation and non-bonded interactions.

Changes in dipole moments (3) and nuclear magnetic resonance chemical shifts (4), when deuterium is substituted for hydrogen, indicate that deuterium is more electropositive than hydrogen. This inductive effect is also observed

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in chemical reactions. Deuterium substitution in the side chain decreases the strength of acids (5) and increases the strength of bases (6). Deuterium substitution on the aromatic ring increases the solvolysis rate of benzhydryl chloride (7).

Deuterium substitution beta to the leaving group in an S_N1 reaction involving a carbonium ion intermediate retards the reaction rate. A typical example is the solvolysis of *t*-butyl chloride- d_9 in water, where $k_H/k_D = 2.387$ and $\Delta\Delta G^\ddagger/n = 58$ cal/mole (8) ($\Delta\Delta G^\ddagger/n$ will be used to compare the magnitude of isotope effects, where $\Delta\Delta G^\ddagger = \Delta G_H^\ddagger - \Delta G_D^\ddagger$ and n is the number of deuterium atoms per molecule). The inductive effect of deuterium cannot account for this isotope effect, as it would increase rather than decrease the reaction rate of the deuterated compound. However, this isotope effect can be explained by hyperconjugation as suggested by Lewis and Boozer (9) and by Shiner (10) when they reported the first beta deuterium isotope effects. The C-H and C-D bond electrons are delocalized by hyperconjugation in the transition state to the incipient carbonium ion. This "weakens" the C-H and C-D bonds and reduces their vibrational frequencies. Therefore, the energy difference in the transition state becomes less than the zero point energy difference in the ground state. Since the C-H bond zero point vibrational energy is greater than that of the C-D bond, the net result is a smaller activation energy for the hydrogen compound than for the deuterium compound.

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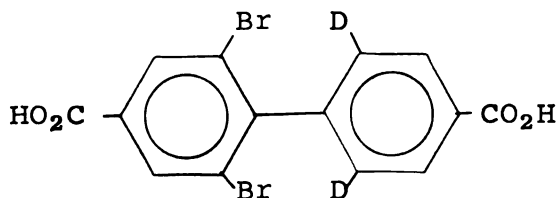
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Bartell (11) has offered an alternative explanation in which he attributes beta deuterium isotope effects to the relief of non-bonded interactions. Since hydrogen has a greater mean amplitude of vibration than deuterium and the tetrahedral ground state is more crowded than the transition state leading to the trigonal carbonium ion, there is greater relief of non-bonded interactions for hydrogen than deuterium while proceeding from the reactant to the carbonium ion. Bartell devised a method to calculate the isotope effects originating from this source and showed that they were of the order of magnitude of the isotope effects which had been reported.

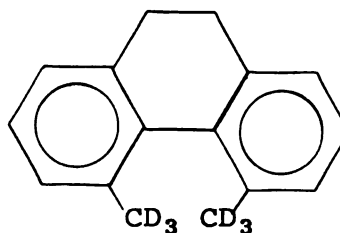
The smaller size of deuterium is demonstrated in the physical properties of deuterated compounds. The molar volume of benzene is 0.8% greater than the molar volume of benzene-d₆ (12). Upon deuteration the carbon-halogen bond lengths of methyl chloride and methyl bromide decrease 0.0008 Å and 0.0011 Å respectively (13).

An elegant demonstration of the lesser steric requirements of deuterium is the isotope effect in the rate of racemization of the biphenyl compounds Ia and Ib.

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Ib

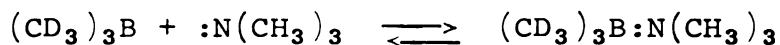


In both cases the deuterated compounds undergo racemization faster as a result of the smaller effective size of deuterium in the sterically crowded transition state. For Ia, $k_D/k_H = 1.19$ (14) and for Ib, $k_D/k_H = 1.13$ (15). The activation energy for the racemization of the protium analog of I has been theoretically calculated by Westheimer to be 18 kcal/mole (16) and by Howlett to be 21.9 kcal/mole (17) in good agreement with the experimental value of 19.0 kcal/mole (18). Melander and Carter (14), by using Bartell's method of calculating steric isotope effects and Westheimer's parameters, obtained a $\Delta\Delta H^\ddagger$ equal to 506 cal/mole, whereas Howlett's parameters led to a $\Delta\Delta H^\ddagger$ of 100 cal/mole. The experimental value of $\Delta\Delta H^\ddagger$ is 90 cal/mole if the isotope effect is considered to be due only to enthalpy differences. The discrepancy in the calculated values is mainly due to the different H--Br potentials that were used by Westheimer and Howlett.

Brown and coworkers have studied the isotope effects on the reactions of 2,6-lutidine in which the methyl groups are deuterated. They find for the reaction of 2,6-dimethyl- d_6 -pyridine with methyl iodide that k_D/k_H is 1.095 (19), corresponding to $\Delta\Delta G^\ddagger = 54$ cal/mole. The reaction of this base with boron trifluoride gives an isotope effect of $\Delta\Delta H^0 = 230$ cal/mole (20), the reaction of the deuterated base being more exothermic. Since no isotope effect was observed for the reactions of methyl iodide and boron trifluoride with pyridine substituted in the 3 and 4 positions

with deuterated methyl groups, the isotope effects of the 2,6-disubstituted pyridine must be due to the smaller steric requirement of the CD_3 group over the CH_3 group. This effect was also found in the partial asymmetric alcoholysis of α -phenylbutyric anhydride with (+)-(S)-2-propanol-1,1,1- d_3 (21).

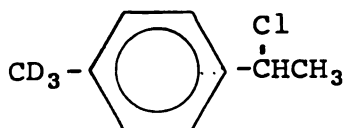
The gas phase equilibrium constant for:



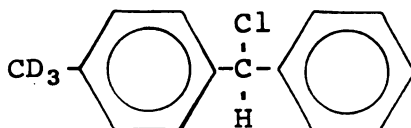
and that of the corresponding hydrogen compounds was determined by Love, Taft and Wartik (22). They estimated the isotope effect to be $\Delta\Delta G^\circ/n = 22$ cal/mole and attributed it to hyperconjugation. Bartell (11) calculated the isotope effect arising from non-bonded interactions to be 20 cal/mole per deuterium. Bartell calculated an isotope effect of 22 cal/mole per deuterium for the solvolysis of *t*-butyl chloride- d_9 , which is less than half of the experimental 58 cal/mole per deuterium.

Most of the earlier work on the elucidation of the origin of secondary beta isotope effects attempted to show that they were due to hyperconjugation. Perhaps the most convincing evidence was the transmission of the isotope effect through an aromatic ring. Acetolysis of IIa gave an isotope effect of $\Delta\Delta G^\ddagger/n = -29$ cal/mole (23)

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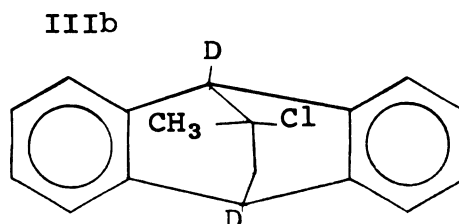
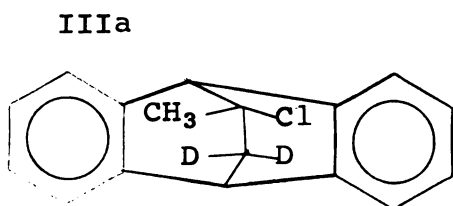
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and solvolysis of IIb in 80% aqueous acetone gave an isotope effect of $\Delta\Delta G^\ddagger/n = -12.4$ cal/mole (24). It would seem unlikely that these isotope effects could be caused by anything other than hyperconjugation. However, this interpretation has been criticized because of the solvent dependence of the isotope effect, as $\Delta\Delta G^\ddagger/n$ is reduced to -2 cal/mole for solvolysis of IIa in 80% acetone-water (25) and to -4.8 cal/mole for solvolysis of IIb in 66.7% acetone-water (24). Isotope effects transmitted through a triple bond have also been reported. For example, $\Delta\Delta G^\ddagger/n = -17$ cal/mole for the solvolysis of 4-chloro-4-methyl-2-pentyne-1,1,1-d₃ in 80% acetone-water and 80% ethanol-water (26).

Hyperconjugation consists of the delocalization of the electrons of a bond into an adjacent vacant p-orbital. It would be expected that hyperconjugation could occur only when the bond is in a suitable orientation for overlap with the p-orbital. Thus a maximum hyperconjugative interaction could be expected when the bond is parallel with the vacant orbital and no hyperconjugative interaction would be expected if the bond is perpendicular to the vacant orbital. Shiner and Humphrey have demonstrated this by the solvolysis of III in 60% ethanol-water (27). Whereas a normal isotope effect, $\Delta\Delta G^\ddagger/n = -49$ cal/mole, is observed for IIIa, a small inverse isotope effect, $\Delta\Delta G^\ddagger/n = 4$ cal/mole, is observed



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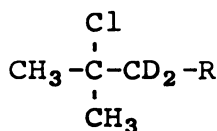
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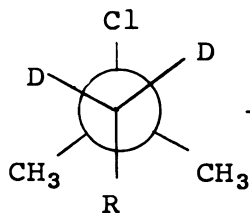
for IIIb. Since the carbon-deuterium bond in IIIb is oriented so that it is perpendicular to the developing p-orbital on the adjacent carbon atom, the only isotope effect is the inductive effect of the deuterium.

Another example of this same type of effect is exhibited in the solvolysis of IV in 80% ethanol-water (28). Shiner

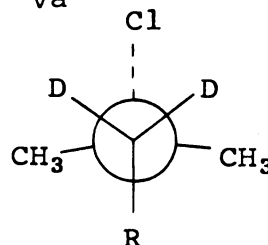
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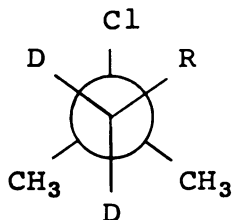
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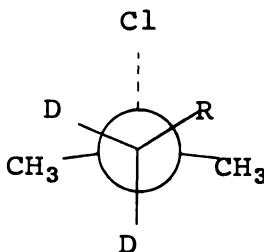
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has found that for R equal to methyl, ethyl, and isopropyl $\Delta\Delta G^\ddagger/n$ equals -102, -101 and -125 cal/mole respectively.

Within experimental error these values are practically identical.

However, when R is a t-butyl group, $\Delta\Delta G^\ddagger/n$ decreases to -27 cal/mole. Shiner interprets this "as characteristic

of the steric prevention of a certain conformation necessary for hyperconjugation". Hyperconjugation should be greater

in transition state Vb, where a deuterium is trans to the

leaving group. Transition state Va should become increasingly more stable relative to Vb as the bulk of the R group

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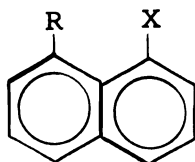
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increases. Thus, when R is t-butyl the preference for conformation Va over Vb greatly increases and as a result the isotope effect decreases sharply.

It seems highly probable, from what has been presented, that both non-bonded interactions and hyperconjugation contribute to secondary beta isotope effects. The relative contribution of each however, is still a subject of some controversy. This question could be resolved by using Bartell's computational method to calculate the steric isotope effect in systems where the isotope effect could originate from both hyperconjugation and non-bonded interactions. First, it would be necessary to determine the validity of Bartell's method of calculation. The obvious choice should be a system where there are steric interactions, but no appreciable hyperconjugation, between the isotopically substituted portion of the molecule and the reaction site. A system fitting these requirements is a 1,8-disubstituted naphthalene (VI) with a carbonyl chloride, acyl chloride or carbomethoxy group in the 1 position and either a deuterium

VI



R = D, CD₃

X = CH₂Cl, COCl, CO₂CH₃

or a methyl-d₃ group in the 8 position. The isotope effect on the hydrolysis of these compounds could be measured and compared with the values calculated by Bartell's method.

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Then, the isotope effect due to non-bonded interactions would be calculated for the hydrolysis of t-butyl chloride, acetyl chloride and ethyl acetate to determine the relative contribution of the steric effect in compounds where hyperconjugation is possible.

EXPERIMENTAL

I. Synthesis

A. Preparation of 8-Methyl-1-naphthoic Acid

The procedure used in the preparation of 8-methyl-1-naphthoic acid was essentially the same as that described by Shone (29). A 300 ml three-necked round-bottomed flask fitted with a reflux condenser, 125 ml dropping funnel and a stirrer was swept with dry nitrogen gas and heated with a flame until dry. After 3.64 g (0.150 g atom) of Domal high purity magnesium was added, the flask was flame dried again, with care being taken to avoid heating the magnesium. About 150 ml of ether was distilled from lithium aluminum hydride directly into the reaction flask. Next, 6.10 g (0.0276 mole) of 8-methyl-1-bromonaphthalene and 5.93 g (0.0542 mole) of ethyl bromide was dissolved in 75 ml of ether which had been removed from the reaction flask with a pipet. This mixture was added dropwise to the stirred ether-magnesium slurry and the resulting solution was refluxed for four hours.

The solution was poured onto 30 g of dry ice and 100 ml of ether was added. After all carbon dioxide evolution had ceased, 20% hydrochloric acid was added along with enough ice to cool the solution until it was acidic. The aqueous and ether layers were separated and the ether layer was washed three times with 75 ml portions of water. The

ether solution was extracted twice with 25 ml portions of 10% sodium hydroxide. The base solution was acidified with 20% hydrochloric acid and the precipitate was removed by filtration. The acid was recrystallized from 30% ethanol to give 3.6 g (70%) of crystals of 8-methyl-1-naphthoic acid.

B. Preparation of 8-Methyl-d₃-1-naphthoic Acid

8-Methyl-d₃-1-naphthoic acid was prepared from 8-methyl-d₃-1-bromonaphthalene by the procedure described for 8-methyl-1-naphthoic acid.

C. Preparation of 8-Methyl-1-naphthylcarbinol

The procedure used in the preparation of 8-methyl-1-naphthylcarbinol is similar to that described by Shone (29). A 300 ml three-necked round-bottomed flask was fitted with a reflux condenser, 125 ml dropping funnel, and a stirrer. Next, 75 ml of dry ether and 2.43 g (0.64 mole) of lithium aluminum hydride were added to the flask. A solution of 6.00 g (0.0322 mole) of ether was added dropwise to the stirred slurry. The mixture was refluxed for forty-eight hours. The flask was cooled in an ice bath and 5 ml of water, followed by 5 ml of 5% sodium hydroxide, was slowly added. The reaction mixture was stirred overnight and then filtered. The aluminum oxide precipitate was washed several times with ether and these washings were added to the filtrate. After evaporation of the ether the alcohol was

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recrystallized from cyclohexane to give 5.0 g (91%) of colorless needles of 8-methyl-1-naphthylcarbinol.

D. Preparation of 8-Methyl-d₃-1-naphthylcarbinol

8-Methyl-d₃-1-naphthylcarbinol was prepared from 8-methyl-d₃-1-naphthoic acid by the procedure described for 8-methyl-1-naphthylcarbinol.

E. Preparation of 8-Methyl-1-naphthylcarbinol- α,α -d₂

8-Methyl-1-naphthylcarbinol- α,α -d₂ was prepared from methyl 8-methyl-1-naphthoate by the procedure described for 8-methyl-1-naphthylcarbinol except for the following modification. A slight excess of lithium aluminum deuteride was used instead of a large excess of lithium aluminum hydride.

F. Preparation of 8-Methyl-1-naphthylcarbiny Chloride

8-Methyl-1-naphthylcarbiny chloride was prepared by essentially the same method as that described by Scheppele (30). Into a 25 ml flask fitted with a reflux condenser was placed 3.37 g (0.0197 mole) of 8-methyl-1-naphthylcarbiny chloride. From the top of the reflux condenser 2.9 ml (0.04 mole) of purified thionyl chloride was slowly added and the resulting solution was refluxed for two hours. The thionyl chloride was stripped off and the 8-methyl-1-naphthylcarbiny chloride was vacuum distilled through a short path distillation head. Recrystallization of the

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distillate from n-hexane gave 3.09 g (82%) of colorless crystals of 8-methyl-1-naphthylcarbiny l chloride, mp 65-66°.

G. Preparation of 8-Methyl-d₃-1-naphthylcarbiny l Chloride

8-Methyl-d₃-1-naphthylcarbiny l chloride was prepared from 8-methyl-d₃-1-naphthylcarbinol by the procedure described for 8-methyl-1-naphthylcarbiny l chloride. The 8-methyl-d₃-1-naphthylcarbiny l chloride was found to have 2.98 deuteriums per methyl group through mass spectral analysis by Seymour Meyerson of the American Oil Company.

H. Preparation of 8-Methyl-1-naphthylcarbiny l Chloride- α,α -d₂

8-Methyl-1-naphthylcarbiny l chloride- α,α -d₂ was prepared from 8-methyl-1-naphthylcarbinol- α,α -d₂ by the procedure described for 8-methyl-1-naphthylcarbiny l chloride.

I. Preparation of 1-Naphthylcarbiny l Chloride

1-Naphthylcarbiny l chloride was prepared from 1-naphthylcarbinol by the method previously described for 8-methyl-1-naphthylcarbiny l chloride.

II. Kinetics

A. Conductance Apparatus

Conductance Bridge. The conductivity measurements were taken with a Wayne Kerr Universal Bridge, model B221 (The Wayne Kerr Laboratories Limited, Surrey, England). The bridge measures conductance together with capacitance or inductance with an accuracy of 0.1%.

Conductance Cell. The conductance cell used was similar to that described by Murr (31). It is described in detail by Papaioannou (32). The procedure recommended by Jones and Bollinger (33) was used to platinize the electrodes. A solution of 0.025 N hydrochloric acid containing 0.3% platinic chloride and 0.025% lead acetate was introduced into the cell. A current of 7 ma was run through the cell for ninety seconds in each direction. The conductance cell was then filled with a solution of 4% sulfuric acid and this solution was electrolyzed for ten minutes in each direction. The cell was cleaned with hot concentrated nitric acid as described by Murr (31).

B. Constant Temperature Bath

The constant temperature bath which was used is described in detail by Papaioannou (32).

C. Calibration of Beckmann Differential Thermometers

The Beckmann differential thermometers were calibrated with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards.

D. Preparation of Solvents

Conductivity Water. The conductivity water was prepared by passing distilled water through a column filled with Dowex 3, anion exchange resin, and Dowex 50W-X8, cation exchange resin. The conductivity water prepared in this manner had a specific conductance of about 3×10^{-6} mho/cm.

Acetone. Purified acetone was prepared by the method of Conant and Kirner (34). The acetone was distilled from potassium permanganate and sodium hydroxide through a 40-cm column fitted with a glass helix. For experimental work only the middle fraction was taken. The specific conductivity of acetone obtained was less than 1×10^{-8} mho/cm.

Mixed Solvent. The solvent used for the kinetic runs was 2/1 acetone-water (V/V). It was prepared for each kinetic run by adding with a pipet two parts of acetone and one part water to the conductance cell.

E. Calibration of Conductance Cell

Preparation of Standard Hydrochloric Acid Solution.

A 0.1 N sodium hydroxide solution was prepared with Fisher Certified Reagent sodium hydroxide. This solution was standardized with Fisher Primary Standard potassium hydrogen phthalate using phenolphthalein as the indicator. A 0.1 N hydrochloric acid 66.67% acetone-water (V/V) solution was prepared and standardized with the standard sodium hydroxide solution by using phenolphthalein as the indicator. A 0.01 N hydrochloric acid solution was then prepared by a ten fold dilution of the 0.1 N hydrochloric acid solution with 66.67% acetone-water (V/V).

Determination of the Volume of the Solvent. The solvent used for the kinetic runs and the cell calibration was prepared by adding 140 ml of purified acetone and 70 ml of

conductivity water to the conductance cell with a 50 ml pipet and a 20 ml pipet. From the density of acetone at 25° (0.7844 g/ml, (35)), the density of water at 25° (0.997044 g/ml, (36)) and the volume of the calibrated pipets that were used, it was calculated that the solvent was 61.14% acetone-water (w/w). The density of the solvent was determined by the following expression:

$$d = d_w + AP_s + BP_s^2 + CP_s^3$$

where d is the density of a solution of P_s percent acetone-water (w/w) and d_w is the density of water. The constants used at 15° were $A = -1.009 \times 10^{-3}$, $B = -9.682 \times 10^{-6}$ and $C = -6.24 \times 10^{-9}$; at 25° $A = -1.171 \times 10^{-3}$, $B = -9.04 \times 10^{-6}$ and $C = -5.6 \times 10^{-9}$ (37). The volume of the solvent was then determined from the density and the weight of the solvent.

Determination of Hydrochloric Acid Concentration as a Function of Conductance. The solvent was added to the conductance cell which was placed in the constant temperature bath. After the temperature of the cell had equilibrated with that of the bath the conductance of the solvent was measured. Then standardized 0.01 N hydrochloric acid solution was added in increments from a 10 ml buret. The solution was stirred for a short time after each addition of the hydrochloric acid solution and the conductance was measured. Thus, about fifteen values of the conductance of a known concentration of hydrochloric acid were obtained

over the range in which readings were taken in the kinetic runs. Two computer programs were written to use the method of least squares to determine hydrochloric acid concentration as a function of conductance. One determined the parameters of a linear relationship and one the parameters of a cubic relationship.

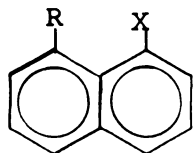
F. Kinetics of Solvolysis

After the conductance cell was filled with solvent, placed in the temperature bath, and attained temperature equilibrium, the solvent conductance was measured. About 0.2 g of chloride was weighed on a Mettler balance in a one milliliter cup. The cup was then dropped into the conductance cell and the solution was stirred for about fifteen minutes to completely dissolve the chloride. The timer was started when the chloride was added to the cell. When the conductance of the solution reached 10^{-4} mho, readings of conductance and time were initiated. Fifteen to twenty readings were taken over a period of three to twelve hours, depending upon the reaction rate. The first order rate constant was then obtained from the appropriate kinetic expression.

RESULTS

The rates of solvolysis of VIIa, VIIb, VIIc and VIId were measured by a conductometric technique in 66.67%

VII



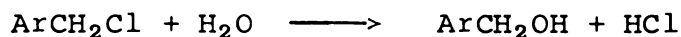
VIIa $R=CH_3$, $X=CH_2Cl$

VIIb $R=CD_3$, $X=CH_2Cl$

VIIc $R=H$, $X=CH_2Cl$

VIId $R=CH_3$, $X=CD_2Cl$

acetone-water (V/V). The alkyl chloride reacts with water to form an alcohol and aqueous hydrogen chloride. Since



the equivalent conductance of the hydrogen chloride is much greater than that of any other species present, the rate of reaction was followed by measuring the rate of appearance of hydrogen chloride by conductance.

The integrated first order rate expression is:

$$\ln(C_0 - [HCl]) = -kt + \ln C_0$$

where C_0 is the initial naphthylcarbinyll chloride concentration, k is the first order rate constant and $[HCl]$ is the concentration of hydrochloric acid at time t . This expression could have been considerably simplified if it would have been possible to measure the conductance at infinite time. This was not practical because the half-life of the reaction was two and one half days. Thus it was necessary to determine the initial concentration of the chloride and the concentration of hydrochloric acid corresponding to each observed conductance reading.

The initial concentration of the naphthylcarbinyll chloride was determined by weighing out a sample for each kinetic run. The concentration of hydrochloric acid as a function of conductance was found by adding increments of a standardized hydrochloric acid solution to a known volume of the solvent in the conductance cell and measuring the conductance after each addition. The data of one of these cell standardizations are given in Table 1. The method of least squares was then used to fit the concentration of hydrochloric acid ($[HCl]$) to the corresponding values of the conductance of the solution (L) by the linear equation:

$$[HCl] = A + BL.$$

The parameters A and B which were obtained for each cell standardization are listed in Table 2.

The kinetic runs were carried out by adding a weighed amount of naphthylcarbinyll chloride to a known volume of the 66.7% acetone-water (V/V) solvent in the conductance cell and then measuring the conductance at various time intervals. The data of a typical kinetic run are tabulated in Table 3. The first order rate constant was then determined from the relationship:

$$\ln(C_0 - A - BL) = -kt + \ln C_0.$$

The slope ($-k$) and the intercept ($\ln C_0$) of a plot of $\ln(C_0 - A - BL)$ vs. t were determined by the method of least squares. The rate constants which were obtained from each kinetic run are listed in Tables 4 and 5. The initial

Table 1. Data of cell standardization 1 at 24.285°

HCl Added ml	Conductance $\times 10^4$ mhos
0	0.006734
2.627	0.5740
3.02	0.6602
3.44	0.7505
3.90	0.8512
4.243	0.9257
4.645	1.0121
4.978	1.0831
5.385	1.172
5.85	1.271
6.22	1.351
6.58	1.426
7.09	1.535
7.54	1.629
8.01	1.728
8.523	1.836
9.00	1.935
9.673	2.070
10.215	2.186
10.72	2.289
11.24	2.395
11.90	2.5275
12.63	2.674
13.36	2.818
14.00	2.944

Table 2. Parameters A and B for the expression
 $[HCl] = A + BL$

T, °C	Volume (ml)	Standardi- zation	A	B
15.496	199.20	1	6.0371×10^{-6}	3.3760
15.496	199.20	2	1.6637×10^{-5}	3.3426
24.285	201.356	1	5.7111×10^{-6}	2.8022
24.285	201.356	2	3.0236×10^{-6}	2.8040
34.558	203.00	1	-1.4954×10^{-6}	2.3198
34.558	203.00	2	-7.0683×10^{-6}	2.3223
34.558	201.81	1	-1.3559×10^{-6}	2.3320
34.558	201.81	2	-5.6618×10^{-7}	2.3345

Table 3. Data for solvolysis of 8-methyl-1-naphthyl-carbinyll chloride in run 6 at 24.285⁰ in 66.67% acetone-water (v/v)

Time (min)	Conductance $\times 10^4$ (mhos)	Calculated k $\times 10^6$ (sec ⁻¹)
272.04	1.0278	3.157
288.70	1.0880	3.160
309.10	1.163	3.167
335.95	1.259	3.168
352.85	1.318	3.166
370.78	1.382	3.168
399.60	1.484	3.170
418.54	1.550	3.170
435.90	1.610	3.169
454.86	1.676	3.169
473.25	1.740	3.170
503.81	1.845	3.170
523.01	1.910	3.168
555.09	2.017	3.164
571.14	2.072	3.165
588.27	2.129	3.163
605.38	2.187	3.164

Initial concentration = 5.5789×10^{-3} mole/l.

Solvent conductance = 9.00×10^{-7} mhos.

k = 3.167 ± 0.003 sec⁻¹.

Table 4. Rate constants and isotope effects for solvolysis of 8-R-1-naphthylcarbinyl chloride in 66.67% acetone-water

Run	R	T, °C	k x 10 ⁶ (sec ⁻¹)	Average k x 10 ⁶ (sec ⁻¹)	k _H /k _D
1	CH ₃	24.285	3.134		
2	CH ₃	24.285	3.122		
3	CH ₃	24.285	3.117		
4	CH ₃	24.285	3.194		
5	CH ₃	24.285	3.087		
6	CH ₃	24.285	3.167		
7	CH ₃	24.285	3.196		
8	CH ₃	24.285	3.140		
9	CH ₃	24.285	3.068		
10	CH ₃	24.285	3.080		
11	CH ₃	24.285	3.084		
12	CH ₃	24.285	3.136	3.127 ± 0.041	
13	CD ₃	24.285	3.036		
14	CD ₃	24.285	3.101		
15	CD ₃	24.285	3.080		
16	CD ₃	24.285	3.106		
17	CD ₃	24.285	3.116	3.088 ± 0.028	1.013 ± 0.022
18	CH ₃	15.496	0.8685		
19	CH ₃	15.496	0.8724		
20	CH ₃	15.496	0.8864		
21	CH ₃	15.496	0.8485		
22	CH ₃	15.496	0.8423		
23	CH ₃	15.496	0.8797		
24	CH ₃	15.496	0.8690	0.8667 ± 0.0148	
25	CD ₃	15.496	0.8435		
26	CD ₃	15.496	0.8658		
27	CD ₃	15.496	0.8683		
28	CD ₃	15.496	0.8845	0.8655 ± 0.0146	1.001 ± 0.034
29	CH ₃	34.558	11.55		
30	CH ₃	34.558	11.45		
31	CH ₃	34.558	11.75		
32	CH ₃	34.558	11.70	11.61 ± 0.012	
33	CD ₃	34.558	11.32		
34	CD ₃	34.558	11.46		
35	CD ₃	34.558	11.49	11.42 ± 0.008	1.017 ± 0.018

Table 5. Rate constants for solvolysis of 1-naphthylcarbinyll chloride and 8-methyl-1-naphthylcarbinyll chloride- α,α -d₂ in 66.67% acetone-water (v/v) at 24.285°

Run	$k \times 10^6$ (sec ⁻¹)	Average k $\times 10^6$ (sec ⁻¹)	k_H/k_D
1-Naphthylcarbinyll Chloride			
1	0.103		
2	0.0936	0.098 $\pm$ 0.005	
8-Methyl-1-naphthylcarbinyll Chloride- α,α -d ₂			
1	2.367		
2	2.375		
3	2.341	2.361 $\pm$ 0.014	1.324 $\pm$ 0.025

concentration calculated from the intercept of $\ln C_0$ was generally within 0.2% to 0.3% of the experimental initial concentration for each kinetic run. The standard deviation of the slope or rate constant was less than 0.1% for each kinetic run. The deviations, however, between different runs were considerably greater than this.

One possible source of error could be the not immediate dissolution of the naphthylcarbonyl chloride. When the temperature was about 25°, although most of the chloride dissolved within one minute, it usually took five to six minutes for it to dissolve completely. It is impossible to determine how much this initial concentration gradient would change the rate constant, but the effect would probably not be very great, as conductance readings were not taken until about 300 min had elapsed. No noticeable trend was present in the values of the rate constants from different kinetic runs where the amount of time necessary to dissolve all of the chloride was different.

The reaction is an equilibrium process. Since the kinetic data were taken during the first part of the first half-life of the reaction, the effect of the reverse reaction on the value of the first order rate constant is negligible. An estimate of the equilibrium constant was obtained from the conductance of the solution at infinite time. When this value of the equilibrium constant was used in the appropriate kinetic expression that regarded the reaction to be an equilibrium process, the rate constants were changed by less than 0.02% for each kinetic run.

The conductance cell was standardized twice at each temperature. The average rate constants at each temperature, which were obtained by using the different standardizations, are listed in Table 6. The difference between the average rate constants for the different cell standardizations is negligible except for those at 15° where the difference is 1%. This difference, however, does not change the ratio k_H/k_D . At 15° and 25° the volume of the solvent was calculated as previously described; however, at 35° the volume had to be estimated. Whereas the parameters of the standardization equation changed slightly, as shown in Table 2, when they were calculated from different solvent volumes, the rate constants in Table 6 did not change when they were calculated from the different standardization equations and the different volumes. Consequently, the isotope effect did not change.

In addition to the linear relationship between hydrochloric acid concentration and conductance, the data of the cell standardizations were also fitted to a cubic relationship to see if a better fit might be obtained. The parameters A, B, C and D of the equation:

$$[\text{HCl}] = A + BL + CL^2 + DL^3$$

were obtained by the method of least squares and are listed in Table 7. This expression was used with the kinetic data to calculate the rate constants. In Table 8 the average rate constants obtained by using this cubic expression are compared with those obtained by using a linear relationship.

Table 6. Average rate constants and isotope effects for solvolysis of 8-R-1-naphthylcarbinyl chloride in 66.67% acetone-water (V/V) using different standardizations and initial volumes

R	T, °C	V (ml)	Standardization ¹		Standardization ²	
			$k \times 10^6$ (sec ⁻¹)	k_H/k_D	$k \times 10^6$ (sec ⁻¹)	k_H/k_D
CH ₃	15.496	199.20	0.8667		0.8591	
CD ₃	15.496	199.20	0.8655	1.001	0.8577	1.001
CH ₃	24.285	201.356	3.127		3.127	
CD ₃	24.285	201.356	3.088	1.013	3.088	1.013
CH ₃	34.558	201.81	11.61		11.62	
CD ₃	34.558	201.81	11.42	1.017	11.43	1.017
CH ₃	34.558	203.00	11.61		11.62	
CD ₃	34.558	203.00	11.42	1.017	11.43	1.017

Table 7. Parameters A, B, C and D for the expression
 $[HCl] = A + BL + CL^2 + DL^3$

T, °C	Std.	A	B	C	D
24.285	1	3.1761×10^{-6}	2.8577	-3.5652×10^2	6.8515×10^5
24.285	2	5.5407×10^{-6}	2.7675	1.2082×10^2	-5.8972×10^5
34.558	1	4.9941×10^{-6}	2.2490	2.0716×10^2	-1.3583×10^5
34.558	2	6.2918×10^{-6}	2.2237	3.8554×10^2	-4.6660×10^5

Table 8. Average rate constants for the solvolysis of
 8-R-1-naphthylcarbinyl chloride obtained by using
 the linear and cubic standardization expressions

R	T, °C	Std.	$k \times 10^6 \text{ (sec}^{-1}\text{)}$	
			Linear Std.	Cubic Std.
CH ₃	24.285	1	3.122	3.124
CH ₃	24.285	2	3.127	3.127
CD ₃	24.285	1	3.083	3.084
CD ₃	24.285	2	3.088	3.088
CH ₃	34.558	1	11.61	11.62
CH ₃	34.558	2	11.61	11.62
CD ₃	34.558	1	11.42	11.43
CD ₃	34.558	2	11.42	11.43

The effect on the average rate constants is very small and the isotope effects do not change. The accuracy of the results did not increase with the use of this cubic expression.

The average rate constants at the different temperatures were used to determine the thermodynamic activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ from the relationship:

$$\log(k_r/T) = \frac{-\Delta H^\ddagger}{2.3026R} \left(\frac{1}{T}\right) + \frac{\Delta S^\ddagger}{2.3026R} + \log(k/h)$$

where k_r is the rate constant, T is the absolute temperature, R is the gas constant, k is Boltzmann's constant and h is Planck's constant. The method of least squares was used to determine the slope and intercept of a plot of $\log(k_r/T)$ versus $1/T$, from which the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in Table 9 were obtained. The isotope effects were then calculated at each temperature from the relationship:

$$\Delta\Delta G^\ddagger = -RT \ln(k_H/k_D) = \Delta\Delta H^\ddagger - T\Delta\Delta S^\ddagger.$$

These values of the calculated isotope effects along with the experimental k_H/k_D ratios are listed in Table 10.

Table 9. Activation parameters and isotope effects for the solvolysis of 8-R-1-naphthylcarbinyl chloride in 66.67% acetone-water (v/v)

R	$\Delta H^\ddagger$ kcal/mole	$\Delta S^\ddagger$ cal/deg/mole	$\Delta H^\ddagger_H - \Delta H^\ddagger_D$ kcal/mole	$\Delta S^\ddagger_H - \Delta S^\ddagger_D$ cal/deg/mole
CH ₃	23.42 ± 0.16	-5.03 ± 0.53		
CD ₃	23.28 ± 0.15	-5.52 ± 0.48	0.14 ± 0.31	0.49 ± 1.01

Table 10. Isotope effects calculated from $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ and experimental isotope effects

T, °C	$\Delta G^\ddagger_H - \Delta G^\ddagger_D$ (calc) cal/mole	k_H/k_D (calc)	k_H/k_D (exp)
15.496	-2	1.003	1.001
24.285	-6	1.010	1.013
34.558	-11	1.018	1.017

CALCULATION OF ISOTOPE EFFECTS

I. Method of Calculation

A. General Theory

The numerical calculation of isotope effects due to non-bonded interactions was done by the method introduced by Bartell (11). His model requires the following assumptions:

1. The potential energy of non-bonded interactions between atoms depends only on the distance, r , between the atoms and can be approximated by a potential function $V(r)$.

2. Substitution of deuterium for hydrogen in a molecule does not affect the mean distance, r_g , between atom pairs.

3. The time average probability distribution describing the separation of atoms is of the form:

$$P(x) = k \exp(-x^2/2l_t^2) \quad \underline{1}$$

where $x = r - r_g$, and l_t^2 is the mean square amplitude of vibration of the atom pair.

4. l_t can be subdivided into l_m and l_s by the relationship:

$$l_t^2 = l_m^2 + l_s^2 \quad \underline{2}$$

where l_m^2 is the component of the mean square amplitude of vibration which arises from the zero point motion of the hydrogen atom and is dependent upon it's mass and l_s is

the component which arises from other skeletal vibrations and is independent of the mass of the hydrogen.

5. Since ℓ_m^2 is mass sensitive it will vary inversely as the square root of the reduced mass giving:

$$\ell_m(\text{H})/\ell_m(\text{D}) \simeq 1.17 \quad \underline{3}$$

If $V(r)$ is a weak interaction coupling oscillators of amplitude ℓ_m and ℓ_s , the average potential energy of each non-bonded interaction then becomes:

$$\bar{V}(r_g) \simeq \iint V(r) P_m(x_m) P_s(x_s) dx_m dx_s \quad \underline{4}$$

$V(r)$ is expanded in a Taylor's series about the mean separation, r_g , and substituted into 4. Integration then results in the following expression for each interaction:

$$\bar{V}_{ij}(r_g) \simeq [V(r_g) + \ell_t^2 V''(r_g)/2 + \ell_t^4 V^{1V}(r_g)/8 + \dots]_{ij} \quad \underline{5}$$

The component of the activation energy resulting from non-bonded interactions, ΔV , can be expressed as the difference in the potential energy due to non-bonded interactions between the transition state and the ground state:

$$\Delta V = \Sigma \Delta \bar{V}_{ij} = \bar{V}_{ij}(r_g, \text{t.s.}) - \Sigma \bar{V}_{ij}(r_g, \text{g.s.}) \quad \underline{6}$$

The isotope effect due to non-bonded interactions, $\Delta\Delta E$, is:

$$\Delta\Delta E = \Delta V(\text{H}) - \Delta V(\text{D}) \quad \underline{7}$$

Substitution of expressions 5 and 6 into equation 7 results in:

$$\Delta\Delta E \simeq [\ell_t^2(\text{H}) - \ell_t^2(\text{D})] \Sigma \Delta V_{ij}''/2 + [\ell_t^4(\text{H}) - \ell_t^4(\text{D})] \Sigma \Delta V_{ij}^{1V}/8 + \dots \quad \underline{8}$$

where: $\Delta V_{ij}'' = V_{ij}''(r_g, \text{t.s.}) - V_{ij}''(r_g, \text{g.s.})$

$$\Delta V_{ij}^{1V} = V_{ij}^{1V}(r_g, \text{t.s.}) - V_{ij}^{1V}(r_g, \text{g.s.})$$

By using equations 2 and 3, the expression simplifies to approximately:

$$\Delta \Delta E \simeq 0.135 l_m^2(H) \Sigma [\Delta V_{ij}'' + l_t^2(H) \Delta V_{ij}^{1V}/2] \quad \underline{9}$$

Bartell used the additional assumption for the H-H and C-H potential functions which he used (38):

$$V''/2V^{1V} \simeq 15 \times 10^{16} \text{ cm}^{-2}$$

This further simplifies expression 9 to:

$$\Delta \Delta E \simeq 0.135 l_m^2(H) \Sigma [1 + 15 \times 10^{16} l_t^2(H)]_{ij} \Delta V_{ij}'' \quad \underline{10}$$

Thus the parameters necessary to calculate the isotope effect are $V''(r_g)$, $V^{1V}(r_g)$, l_m and l_t for each interaction.

B. Interatomic Distances

Structural data were available for some of the compounds of interest. Where they were not available the structure was estimated from similar compounds whose structure was known. The structures that were used are listed in the Appendix. The interatomic distances were determined from the polar coordinates of the atoms of the molecule by means of a computer program supplied by Dr. R. Schwendeman of this department.

C. Potential Functions

The potential functions of Bartell (38), Scott and Scheraga (39) and Hendrickson (40) were used. These are of

the form:

$$V(r) = A \exp(-Br) - Cr^{-6}$$

and are listed in Table 11. A computer program was written that evaluated each of these functions and their second and fourth derivatives every 0.01 Å from 1.50 Å to 3.50 Å. These values were then used in equation 9. Bartell did not have an analytic function for H-Cl and H-O interactions and merely made a graphical estimate of the second derivative for these interactions. Thus, when using Bartell's potential functions, the second derivatives of the potential functions for H-Cl, H-C and H-O interactions were estimated graphically and equation 10 was used to calculate the isotope effect. When possible, the isotope effects for each compound were calculated by using both the potential functions of Bartell and those of Scott and Scheraga.

D. Mean Square Amplitudes of Vibration

The values of ℓ_m used were 0.09 Å and 0.10 Å for H-X interactions and 0.12 Å to 0.135 Å for H-H interactions, to correspond with the values suggested by Bartell (11). Values of ℓ_t can be obtained by electron diffraction studies, but no structure determination of the compounds of interest has been done by electron diffraction. The magnitude of ℓ_t was estimated for each interaction, by using as a basis the values tabulated by Morino and coworkers (41). The values used in each case are listed in the Appendix.

Table 11. Parameters of the non-bonded potential function
 $V(r) = A \exp(-Br) - Cr^{-6}$ for $V(r)$ in calories/
 mole and r in angstroms.

Author	Ref.	Inter- action	A	B	C
Scott and Scheraga	39	H--H	9.17×10^6	4.54	4.52×10^4
Scott and Scheraga	39	H--F	1.69×10^7	4.57	6.27×10^4
Scott and Scheraga	39	H--Cl	3.90×10^7	4.15	3.21×10^5
Scott and Scheraga	39	H--Br	2.18×10^7	3.66	4.65×10^5
Scott and Scheraga	39	H--O	2.68×10^7	4.57	9.04×10^4
Scott and Scheraga	39	H--O ^a	3.46×10^7	4.57	1.22×10^5
Hendrickson	40	H--C	1.29×10^7	4.12	1.25×10^5
Bartell	38	H--H	6.59×10^7	4.082	4.92×10^4

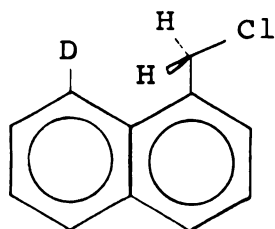
^aWhere the oxygen atom is a carbonyl oxygen.

II. Calculation of Isotope Effects

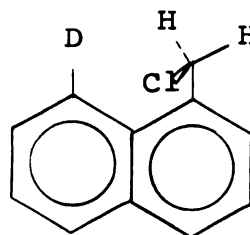
A. 1-Naphthylcarbinyl Chloride-8-d

The isotope effects of 1-naphthylcarbinyl chloride-8-d summarized in Table 12 were calculated for two different ground state conformations and five different conformations of the transition state, which was assumed to be a carbonium ion. The ground state conformations used were VIII and IX,

VIII



IX



where the CH_2Cl group in IX was rotated six degrees in the direction that increased the distance between the peri-hydrogen and the chlorine atom. The potential functions of Scott and Scheraga (39) were used to calculate the energy of the interactions of the CH_2Cl group with the hydrogens in the ortho and peri positions for each conformation. Conformation IX, when rotated six degrees, was found to be about 450 cal more stable than VIII. Various angles of deviation, θ , of the CH_2 group from coplanarity with the ring were used for the conformation of the carbonium ion.

B. 8-Methyl- d_3 -1-naphthylcarbinyl Chloride

Conformation X was used for the ground state of 8-methyl- d_3 -1-naphthylcarbinyl chloride. The carbonium ion, XI, that

Table 12. Calculated isotope effects for 8-R-1-naphthyl-carbinyl chlorides

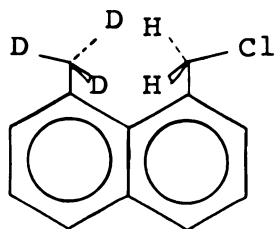
R	Conf.	θ degrees	ϕ degrees	$v(r)^a$ from	$\Delta E_H - \Delta E_D$ cal/mole	k_H/k_D 25 ^o D
D	I	0		B	39	0.93
D	I	15		B	29	0.95
D	I	30		B	12	0.98
D	I	45		B	- 2	1.003
D	I	90		B	-15	1.03
D	I	0		S	30	0.95
D	I	15		S	22	0.96
D	I	30		S	10	0.98
D	I	45		S	0	1.00
D	I	90		S	- 7	1.01
D	II	0		B	-26	1.04
D	II	15		B	-36	1.06
D	II	30		B	-54	1.10
D	II	45		B	-67	1.12
D	II	90		B	-80	1.14
D	II	0		S	21	0.96
D	II	15		S	14	0.98
D	II	30		S	1	1.00
D	II	45		S	- 9	1.01
D	II	90		S	-16	1.03
CD ₃		0	0	B	70	0.89
CD ₃		15	7	B	49	0.92
CD ₃		30	12	B	0	1.00
CD ₃		45	16	B	-45	1.08
CD ₃		90	0	B	-55	1.10
CD ₃		0	0	S	59	0.90
CD ₃		15	7	S	40	0.93
CD ₃		30	12	S	0	1.00
CD ₃		45	16	S	-33	1.06
CD ₃		90	0	S	-40	1.07
C(CD ₃) ₃		0		S	-48	1.08

^aB denotes Bartell

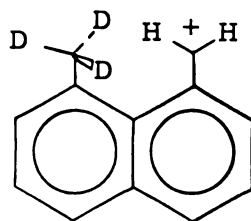
S denotes Scott and Scheraga

was assumed for the transition state, was twisted different angles, θ , from the plane of the ring. For each of these transition state conformations the 8-methyl group was rotated ϕ degrees to maximize the distance between the hydrogen atoms of the carbonium ion and those of the methyl group. The isotope effects are listed in Table 12.

X



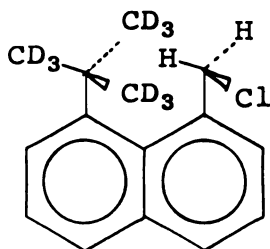
XI



C. 8-t-Butyl-d₉-1-naphthylcarbiny Chloride

Conformation XII was used for 8-t-butyl-d₉-1-naphthylcarbiny chloride and also for the corresponding carbonium ion, which was assumed to be planar with the ring. The

XII



methyl groups were rotated so that their hydrogens were at a maximum distance from the nearest hydrogen on the CH₂Cl group or on the CH₂ group. This amounted to a rotation from the normal staggered conformation of the t-butyl group of 38° for the chloride and 35° for the cation. The calculated isotope effect is listed in Table 12.

Table

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XIV

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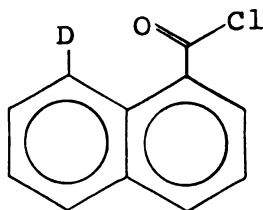
The

tion.

D. 1-Naphthoyl Chloride-8-d

The isotope effects of 1-naphthoyl chloride-8-d in Table 13 were calculated for ground state conformation XIII, in which the COCl group is planar with the aromatic ring, and for conformations in which the COCl group deviated

XIII

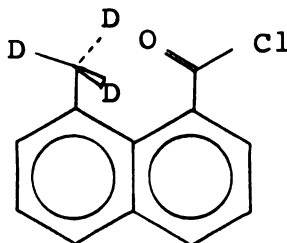


θ degrees from coplanarity. In each case the transition state was taken as the linear acylium ion.

E. 8-Methyl-d₃-1-naphthoyl Chloride

The isotope effects of 8-methyl-d₃-1-naphthoyl chloride in Table 13 were calculated for ground state conformation XIV and for other conformations with various dihedral angles, θ , between the plane of the COCl group and the plane of the ring. For each non-planar conformation, the methyl group was rotated ϕ degrees to maximize the distance between

XIV



the hydrogens of the methyl group and the carbonyl oxygen. The linear acylium ion was again assumed to be the transition state.

Table 13. Calculated isotope effects for 8-R-1-naphthoyl chlorides

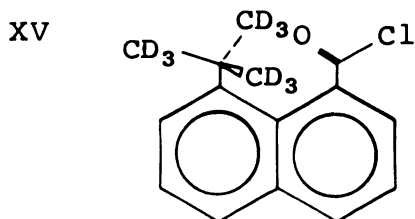
R	θ degrees	ϕ degrees	$V(r)^a$ from	$\Delta E_H - \Delta E_D$ cal/mole	k_H/k_D (25°C)
D	0		B	-318	1.71
D	15		B	-254	1.52
D	30		B	-159	1.31
D	45		B	- 58	1.10
D	90		B	0	1.00
D	0		S	-183	1.36
D	15		S	-147	1.28
D	30		S	- 76	1.14
D	45		S	- 29	1.05
D	90		S	0	1.00
CD ₃	0	0	B	-870	4.31
CD ₃	15	7.5	B	-710	3.32
CD ₃	30	14	B	-460	2.17
CD ₃	45	18	B	-250	1.52
CD ₃	60	20	B	-116	1.21
CD ₃	70	20	B	- 90	1.16
CD ₃	90	0	B	- 65	1.12
CD ₃	0	0	S	-530	2.43
CD ₃	15	7.5	S	-420	2.03
CD ₃	30	14	S	-230	1.48
CD ₃	45	18	S	-100	1.18
CD ₃	60	20	S	- 40	1.07
CD ₃	75	20	S	- 20	1.03
CD ₃	90	0	S	- 14	1.02
C(CD ₃) ₃			S	-750	3.52

^aB denotes Bartell

S denotes Scott and Scheraga.

F. 8-t-Butyl-d₉-1-naphthoyl Chloride

The isotope effect of 8-t-butyl-d₉-1-naphthoyl chloride in Table 13 was calculated for the planar ground state conformation XV and a linear acylium ion transition state.



The methyl groups were again rotated to maximize the non-bonded distances as was done for 8-t-butyl-1-naphthylcarbonyl chloride. The angle of rotation was 30° for the acid chloride and 32° for the acylium ion.

G. Methyl 1-Naphthoate-8-d and Methyl 8-Methyl-d₃-1-naphthoate

The isotope effects in Table 14 were calculated for the basic hydrolysis of the naphthoate esters. The ground state conformations used for methyl 1-naphthoate-8-d were the same as those used for 1-naphthoyl chloride-8-d and the ground state conformations used for methyl 8-methyl-d₃-1-naphthoate were the same as those used for 8-methyl-d₃-1-naphthoyl chloride, except that in both cases the chlorine atom was replaced by a methoxy group. The transition states were assumed to be tetrahedral and to have conformation XVI and XVII, respectively.

Table 14. Calculated isotope effects for the basic hydrolysis of methyl 8-R-1-naphthoates

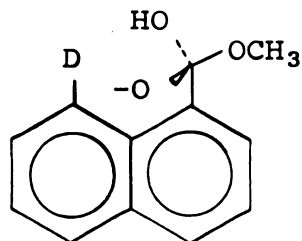
R	θ degrees	ϕ degrees	$v(r)^a$ from	$\Delta E_H - \Delta E_D$ cal/mole	k_H/k_D (25°C)
D	0		B	-270	1.57
D	15		B	-206	1.42
D	30		B	-111	1.21
D	45		B	- 10	1.02
D	90		B	50	0.92
D	0		S	-162	1.31
D	15		S	-126	1.23
D	30		S	- 55	1.09
D	45		S	- 8	1.01
D	90		S	12	0.98 ^b
CD ₃	0	0	B	-338	1.61 ^b
CD ₃	15	7.5	B	-171	1.27 ^b
CD ₃	30	14	B	75	0.90 ^b
CD ₃	45	18	B	279	0.67 ^b
CD ₃	60	20	B	419	0.55 ^b
CD ₃	70	20	B	466	0.51 ^b
CD ₃	90	0	B	504	0.49 ^b
CD ₃	0	0	S	-252	1.43 ^b
CD ₃	15	7.5	S	-157	1.25 ^b
CD ₃	30	14	S	29	0.96 ^b
CD ₃	45	18	S	165	0.79 ^b
CD ₃	60	20	S	230	0.72 ^b
CD ₃	75	20	S	246	0.70 ^b
CD ₃	90	0	S	256	0.69 ^b

^aB denotes Bartell

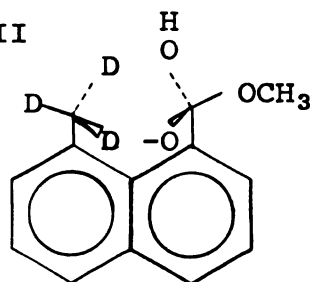
S denotes Scott and Scheraga.

^b78°.

XVI



XVII



H. t-Butyl Chloride-d₉

The isotope effects for the solvolysis of t-butyl chloride-d₉ (Table 15) were calculated to attempt to duplicate Bartell's calculations. The staggered C_{3v} conformation was used for the chloride and the C_{3h} conformation for the carbonium ion.

I. Acetyl Chloride-d₃

The most stable conformation of acetyl chloride has been shown by microwave spectroscopy (42) to be the one where the carbonyl group is eclipsed by a hydrogen of the methyl group. The linear acylium ion was taken as the transition state. X-ray crystallography studies have shown that the carbon-carbon bond in CH₃COSbF₆ is shorter in the acylium ion (43) than in acetyl chloride by 0.12 Å. This introduces a large C-H interaction into the calculated isotope effects (Table 15). Since the non-bonded interactions with the hydrogen atoms are not as great for the positively charged carbon atom in the cation as for the carbon atom in acetyl chloride, the increased interactions due to the bond shortening in the cation will be somewhat canceled out. Therefore

Table 15. Other calculated isotope effects

Compound	$v(r)^a$ from	$\Delta E_H - \Delta E_D$ cal/mole	k_H/k_D (25°C)
$(CD_3)_3CCl$	B	-198 ^b	1.39 ^b
	B	-186	1.36
	S	- 43	1.07
CD_3COCl	B	29	0.94 ^d
	S	8.1	0.99 ^d
	B	- 38 ^c	1.08 ^d
	S	- 8.6 ^c	1.02 ^d
$CD_3CO_2C_2H_5$	B	20	0.97
	S	5	0.99
$C-CD_2Cl$	B	-637	2.92
	S	-130	1.25
2,6-Dimethyl- d_3 -pyridine BF_3 adduct	S	95	
2,6-Dimethyl- d_3 -pyridine BH_3 adduct	B	71	
	S	43	
2,2'-Dibromo-4,4'-dicarboxy- biphenyl-6,6'- d_2	S	60	

^aB denotes Bartell
S denotes Scott and Scheraga.

^bResults of Bartell in Reference 11.

^cNeglecting C-H interactions.

^d-22°.

the isotope effect for acetyl chloride- d_3 was also calculated by omitting all C-H interactions.

J. Ethyl Acetate- d_3

The ground state conformation of ethyl acetate was assumed to be analogous to that of acetyl chloride, i.e. a hydrogen eclipsing the carbonyl. The transition state was assumed to be tetrahedral with the methyl group in a staggered conformation. The isotope effects calculated for the basic hydrolysis of ethyl acetate- d_3 are listed in Table 15.

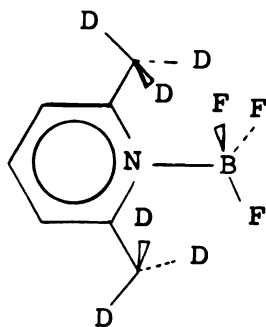
K. Alpha Isotope Effect

The alpha isotope effect listed in Table 15 was calculated for a tetrahedral C- CD_2Cl group ionizing to the corresponding trigonal carbonium ion. All other possible interactions were neglected.

L. Adducts of 2,6-Dimethyl- d_3 -pyridine

The steric isotope effects were calculated for the BH_3 and BF_3 addition products of 2,6-dimethyl- d_3 -pyridine and are listed in Table 15. Conformation XVIII was used for both adducts. Since the boron atom in this addition compound is isoelectronic with carbon, a C-H potential function was used for the B-H interactions.

XVIII



M. 2,2'-Dibromo-4,4'-dicarboxybiphenyl-6,6'-d₂

The isotope effects for the rate of racemization of 2,2'-dibromo-4,4'-dicarboxybiphenyl-6,6'-d₂ (Table 15) were calculated by using the potential function of Scott and Scheraga (39) for H-Br interactions. The hydrogen-bromine distance of 2.31 Å calculated by Westheimer (16) was used for the H-Br interaction in the transition state. The ground state was considered to have no significant interaction.

DISCUSSION

In order to assess the reliability of Bartell's method of calculating isotope effects due to non-bonded interactions (11), the calculated values of the isotope effects will be compared with the experimental values. No attempt will be made to determine the validity of the assumptions, such as the approximation that vibrations are harmonic, which were made in the derivation of his expression. The accuracy of the empirical parameters used in his model, such as the potential functions, will however, be discussed, though in a pragmatic manner.

The racemization of 2,2'-dibromo-4,4'-dicarboxybiphenyl-6,6'-d₂ is a reaction for which the structure of the transition state is known with some certainty. As already mentioned in the introduction, Melander and Carter (14), by using Bartell's method, calculated an isotope effect of 506 cal/mole from Westheimer's (16) H-Br potential function and one of 100 cal/mole from Howlett's (17). Their experimental isotope effect was 90 cal/mole. The isotope effect calculated from the Scott and Scheraga (39) H-Br potential function is 60 cal/mole. Thus it is evident that although Bartell's method appears to be valid for the calculation of isotope effects due to non-bonded interactions, the magnitude of the calculated isotope effect is strongly dependent upon the potential function used.

Another reaction for which the change in interatomic distances can be estimated to a reasonable degree of accuracy is the isotope effect on ΔH^0 for the addition of boron trifluoride and diborane to 2,6-dimethyl-d₃-pyridine. There are no relevant non-bonded interactions in the reactants and reasonable estimates can be made for the structure of the products. The calculated isotope effect for the boron trifluoride addition complex is $\Delta\Delta E = 95$ cal/mole by using the H-F potential function of Scott and Scheraga. This agrees within the limits of experimental uncertainty with the experimental isotope effect of $\Delta\Delta H^0 = 230 \pm 150$ cal/mole (20). The observed isotope effect on the addition of diborane to 2,6-dimethyl-d₃-pyridine (20) is $\Delta\Delta H^0 = -20 \pm 80$ cal/mole. The isotope effect calculated by using Bartell's H-H potential function is $\Delta\Delta E = 71$ cal/mole and that calculated by using Scott and Scheraga's is $\Delta\Delta E = 43$ cal/mole. Conceivably, the H-H potential function of the latter authors may be slightly better.

In S_N¹ reactions where deuterium is substituted for hydrogen on the carbon bearing the leaving group, an alpha isotope effect is observed. Here the non-bonded distances in the ground state can be accurately determined, but the structure of the transition state is unknown. For a C-CD₂Cl group, if the corresponding carbonium ion is considered to be the transition state, the calculated isotope effect is $\Delta\Delta E = -640$ cal/mole by using the potential functions of Bartell and $\Delta\Delta E = -130$ cal/mole by using the potential

functions of Scott and Scheraga. The latter is in good agreement with the observed alpha isotope effect ($\Delta\Delta G^\ddagger = -165$ cal/mole) for 8-methyl-1-naphthylcarbinyl chloride- α,α -d₂. The large alpha isotope effect predicted with Bartell's potential functions is mainly due to the magnitude of the H-Cl interaction. Thus it would seem that the Scott and Scheraga potential functions, or at least their H-Cl potential function, are more realistic.

No significant isotope effect was found (30) for the solvolysis of 1-naphthylcarbinyl chloride-8-d in 0.32 M water-formic acid solution ($k_H/k_D = 1.00 \pm 0.05$ and $\Delta\Delta G^\ddagger = 0 \pm 29$ cal/mole). The reaction exhibits an alpha isotope effect $k_H/k_D = 1.35$ (30), so it is probably S_N1. The carbonium ion assumed for the transition state is probably very close to being planar with the aromatic ring, because on deviation from coplanarity the increase in energy of the system due to decreased delocalization of charge is much greater than the decrease in energy obtained by relieving the non-bonded interactions. For a dihedral angle of 15° simple HMO calculations predict a loss of resonance energy of 2,700 cal/mole, whereas the energy decrease from the alleviation of non-bonded interactions is only 300 cal/mole. As can be seen from Table 12, the calculated isotope effects for a planar carbonium ion and for one with a dihedral angle of 15° are 39 cal/mole and 29 cal/mole respectively by using Bartell's potential functions and 30 cal/mole and 22 cal/mole respectively by using Scott and Scheraga's potential functions, if the chlorine atom is

anti to the peri hydrogen in the ground state conformation (conformation X). If ground state conformation XI is the minimum energy one, the isotope effects calculated by using Bartell's potential functions are -26 cal/mole and -36 cal/mole respectively and those calculated by using Scott and Scheraga's are 21 cal/mole and 14 cal/mole. All of these calculated isotope effects, irrespective of the ground state and carbonium ion conformations, fall within the limits of experimental uncertainty.

The isotope effect for the solvolysis 8-methyl-d₃-1-naphthylcarbinyll chloride in 66.67% acetone-water (V/V) is $k_H/k_D = 1.013 \pm 0.022$ and $\Delta\Delta G^\ddagger = -8 \pm 13$ cal/mole at 25°. The reaction is S_N1 because it has an alpha isotope effect of $k_H/k_D = 1.32$ and because 8-methyl-1-naphthylcarbinyll chloride reacts at a rate about thirty times greater than 1-naphthylcarbinyll chloride. If the mechanism of solvolysis of both compounds is S_N2, the reaction rate of the 8-methyl-1-naphthylcarbinyll chloride would be slower, not faster than 1-naphthylcarbinyll chloride, because of the greater steric requirements of the former. If the mechanism of solvolysis of 1-naphthylcarbinyll chloride is either S_N1 or S_N2 and 8-methyl-1-naphthylcarbinyll chloride is S_N1, the reaction rate of the latter would be greater, as is observed. The carbonium ion is planar or nearly so. If the dihedral angle of the carbonium ion is 15° the energy increase of the system due to decreased overlap (2,700 cal/mole) is much greater than the energy decrease due to alleviation of non-bonded interactions (800 cal/mole).

For dihedral angles of 0° and 15° between the planes of the carbonium ion and the aromatic ring, the isotope effects calculated by using Bartell's potential functions are 70 cal/mole and 49 cal/mole respectively and those calculated by using Scott and Scheraga's potential functions are 59 cal/mole and 40 cal/mole. Thus the calculated isotope effects are not at all in accord with the experimental $\Delta\Delta G^\ddagger$ and are in fact in the opposite direction. However, the calculated isotope effects do agree with the experimental $\Delta\Delta H^\ddagger = +140 \pm 300$ cal/mole. It should be emphasized that any isotope effect originating from non-bonded interactions would effect mainly the enthalpy of activation of the reaction.

The H-H and H-Cl potential functions of both Bartell and Scott and Scheraga seem to give reasonable estimates of the isotope effects for the solvolysis of 1-naphthylcarbinyl chloride-8-d and 8-methyl-d₃-1-naphthylcarbinyl chloride. Those of Scott and Scheraga would be preferred on the basis of their prediction of the alpha isotope effect. However, the isotope effect calculated with these functions for the solvolysis of t-butyl chloride-d₉, a system where hyperconjugation is possible, is much less than the experimental isotope effect. For example, the Scott and Scheraga potential functions give $\Delta\Delta E = -43$ cal/mole, whereas the experimental isotope effect is $\Delta\Delta H^\ddagger \simeq \Delta\Delta G^\ddagger = -516$ cal/mole (8). The isotope effect calculated by using Bartell's potential functions, $\Delta\Delta E = -186$ cal/mole, is closer but

still considerably less than the observed isotope effect.

No significant isotope effect was found for the basic hydrolysis of methyl 1-naphthoate-8-d, where $\Delta\Delta G^\ddagger = -0.6 \pm 4$ cal/mole (32). For this to agree with the calculated isotope effects in Table 14, the dihedral angle of the carbo-methoxy group with the aromatic ring would have to be at least 45° . This assumption is unlikely in view of the fact that the dihedral angle in 1-naphthoic acid is only 11° (44). Since a negative charge is developing in the transition state the interaction between the negatively charged oxygen and the peri hydrogen is probably greater than the value obtained from the O-H potential function. This would have the effect of decreasing the dihedral angle for which no isotope effect is found. No conclusions should be drawn, however, until $\Delta\Delta H^\ddagger$ for this reaction is determined.

The experimental isotope effect for the basic hydrolysis of methyl 8-methyl-d₃-1-naphthoate (47) is $k_H/k_D = 0.89 \pm 0.22$ and $\Delta\Delta G^\ddagger = 82 \pm 15$ cal/mole at 78.5° . The value of $\Delta\Delta H^\ddagger$ determined from the rate constants at this and one other temperature is 800 ± 400 cal/mole. This value is in accord with the isotope effects calculated by using Bartell's potential function if the dihedral angle is 60° or greater but not with those calculated from the Scott and Scheraga potential functions. However, because of the greater O-H interaction in the negatively charged transition state, a dihedral angle of about 45° may not be unreasonable.

In the basic hydrolysis of ethyl acetate- d_3 , Bender and Feng (45) found an isotope effect of $k_H/k_D = 0.90 \pm 0.01$ and $\Delta\Delta G^\ddagger = 60 \pm 6$ cal/mole at 25° . The isotope effect calculated by using Bartell's potential function is 20 cal/mole and that calculated by using the potential functions of Scott and Scheraga is 5 cal/mole. This isotope effect has been determined by Halevi and Margolin (46) at several other temperatures with rather abnormal results; $k_H/k_D = 1.00 \pm 0.01$ at 0° , 0.93 ± 0.01 at 35° and 1.15 ± 0.09 at 65° . If the isotope effect at 0° is omitted and the lower limit (1.06) of the isotope effect at 65° is taken, a plot of $\ln(k_H/k_D)$ versus $1/T$ yields a reasonable facsimile of a straight line. The value of $\Delta\Delta H^\ddagger$ determined from the slope is about 700 cal/mole, a result that should be treated with caution as it seems too great to be realistic. It is difficult to draw definite conclusions on the basis of these experimental data. It does seem, however, that for ethyl acetate- d_3 the calculated isotope effect is less than the experimental.

The calculated isotope effects (Table 13) for the solvolysis of 1-naphthoyl chloride- $8-d$ are substantial. If a reasonable dihedral angle of 15° is assumed, the calculated isotope effect is $\Delta\Delta E = -254$ cal/mole by using the potential functions of Bartell and $\Delta\Delta E = -147$ cal/mole by using the potential functions of Scott and Scheraga. However, no significant isotope effect was observed (32) at 15° , 25° and 35° , at each temperature $\Delta\Delta G^\ddagger$ being about 0 ± 6 cal/mole.

8-Methyl-1-naphthoyl chloride solvolyzes in acetone-water by an S_N1 mechanism (32). The isotope effect for the solvolysis of 8-methyl- d_3 -1-naphthoyl chloride (32) was found to be $k_H/k_D = 1.030 \pm 0.015$ and $\Delta\Delta G^\ddagger = -18 \pm 9$ cal/mole at 25° in 95% acetone-water (w/w). In this temperature range $\Delta\Delta H^\ddagger$ is equal to -29 ± 243 cal/mole. More accurate results were obtained for this reaction in 75.23% acetone-water (w/w) at lower temperatures. At -27° , $k_H/k_D = 1.127 \pm 0.018$, $\Delta\Delta G^\ddagger = -58 \pm 9$ cal/mole and $\Delta\Delta H^\ddagger = -307 \pm 167$ cal/mole in this temperature range. The experimental value of $\Delta\Delta H^\ddagger$ agrees with the calculated isotope effects if the dihedral angle of the acid chloride group with the plane of the aromatic ring is between 30° and 45° . For dihedral angles of 30° and 45° the isotope effects calculated by using the potential functions of Bartell are -460 cal/mole and -250 cal/mole respectively and those calculated by using the potential functions of Scott and Scheraga are -230 cal/mole and -100 cal/mole. The dihedral angle of the acid chloride group in 8-methyl-1-naphthoyl chloride should be about the same as the dihedral angle of the carbomethoxy group in methyl 8-methyl-1-naphthoate. The isotope effects calculated for these compounds by using Bartell's potential functions are consistent with the experimental $\Delta\Delta H^\ddagger$ if this dihedral angle is about 45° .

The isotope effect for the solvolysis of acetyl chloride- d_3 at -22° was determined by Bender and Feng (45) to $k_H/k_D = 1.62$, $\Delta\Delta G^\ddagger = -240 \pm 25$ cal/mole in 80% acetone-water and $k_H/k_D = 1.51$, $\Delta\Delta G^\ddagger = -206 \pm 25$ cal/mole in 90% acetone-

water. The isotope effect calculated by using the potential functions of Bartell is 29 cal/mole, while the one calculated by using those of Scott and Scheraga is 8.9 cal/mole. The inverse isotope effect results from the increased C-H interaction in the acylium ion where the carbon-carbon bond is considerably shorter than it was in the ground state. If the C-H interaction is neglected, then $\Delta\Delta E = -38$ cal/mole from Bartell's potential functions and $\Delta\Delta E = -8.6$ cal/mole from those of Scott and Scheraga.

The kinetic isotope effect for the solvolysis of acetyl chloride- d_3 was also determined by Papaioannou (47) at several different temperatures to obtain the thermodynamic activation parameters. In 80% acetone-water $\Delta\Delta G^\ddagger = -48 \pm 5$ cal/mole and in 90% acetone-water $\Delta\Delta G^\ddagger = -29 \pm 1$ cal/mole at -22° . In 80% acetone-water $\Delta\Delta H^\ddagger = -225 \pm 76$ cal/mole and in 90% acetone-water $\Delta\Delta H^\ddagger = +285 \pm 140$ cal/mole. It appears that acetyl chloride solvolyzes by a mixed S_N1 - S_N2 mechanism. That the S_N2 contribution is considerable is demonstrated by the relative solvolysis rate of 2,2-dimethylpropanoyl chloride, which is 20 times slower than acetyl chloride in 80% acetone-water and 10 times slower in 90% acetone-water (47). In 90% acetone-water the S_N2 term is predominant and the isotope effect resulting from enthalpy is inverse. In 80% acetone-water the contribution of the S_N1 term has increased so as to give a corresponding normal effect.

The isotope effect for the S_N2 reaction, if it is due to non-bonded interactions, should be similar to that calculated for the basic hydrolysis of ethyl acetate- d_3 . However, the calculated isotope effect for ethyl acetate- d_3 ($\Delta\Delta E = 20$ cal/mole or $\Delta\Delta E = 5$ cal/mole) is much less than the experimental isotope effect ($\Delta\Delta H^\ddagger = 285$ cal/mole) in this case. The isotope effect for a pure S_N1 reaction of acetyl chloride- d_3 is either equal to or greater than the $\Delta\Delta H^\ddagger = -225$ cal/mole in 80% acetone-water, which would mean that again the experimental isotope effect is greater than the calculated isotope effect of $\Delta\Delta E = -38$ cal/mole or -8.6 cal/mole.

It can be concluded that Bartell's method of calculation of secondary isotope effects due to non-bonded interactions can correctly predict the isotope effect if appropriate potential functions are chosen and if the system is such that the sole contribution to the isotope effect is the difference in non-bonded interactions between hydrogen and deuterium. However, if the system is one in which hyperconjugation is possible, the calculated isotope effects are much less than the experimental isotope effects. Therefore hyperconjugation, where possible, certainly contributes to the experimental isotope effect. Although the accuracy of the data makes quantitative predictions difficult, in most systems hyperconjugation probably is the main contributor to the isotope effect.

REFERENCES

1. M. J. Stern and M. Wolfsberg, J. Chem. Phys., 45, 2618 (1966).
2. a) J. Bigeleisen, Ibid., 17, 675 (1949).
b) L. Melander, Arkiv. Kemi, 2, 211 (1950).
3. J. S. Muentzer and V. W. Laurie, J. Chem. Phys., 45, 855 (1966).
4. a) G. V. D. Tiers, J. Am. Chem. Soc., 79, 5585 (1957).
b) G. V. D. Tiers, J. Chem. Phys., 963 (1958).
5. A. Streitwieser, Jr. and H. S. Klein, J. Am. Chem. Soc., 85, 2759 (1963).
6. Wn. Van Der Linde and R. E. Robertson, Ibid., 86, 4505 (1964).
7. A. Streitwieser, Jr., and H. S. Klein, Ibid., 86, 5170 (1964).
8. L. Hakka, A. Queen, and R. E. Robertson, Ibid., 87, 161 (1965).
9. E. S. Lewis and C. E. Boozer, Ibid., 74, 6306 (1952).
10. V. J. Shiner, Jr., Ibid., 74, 2925 (1953).
11. L. S. Bartell, Ibid., 83, 3567 (1961).
12. G. R. Clemon and A. McQuillen, J. Chem. Soc., 1220 (1935).
13. R. H. Schwendeman and J. D. Kelley, J. Chem. Phys., 42, 1132 (1965).
14. L. Melander and R. E. Carter, J. Am. Chem. Soc., 86, 295 (1964).
15. K. Mislow, R. Graeve, A. J. Gordon and G. H. Wahl, Jr., Ibid., 86, 1733 (1964).
16. F. H. Westheimer, J. Chem. Phys., 15, 252 (1947).
17. K. E. Howlett, J. Chem. Soc., 1055 (1960).
18. M. M. Harris and R. K. Mitchell, Ibid., 1905 (1960).
19. H. C. Brown and G. J. McDonald, J. Am. Chem. Soc., 88, 2514 (1966).

20. H. C. Brown, M. E. Azzaro, J. G. Koelling and G. J. McDonald, Ibid., 88, 2520 (1966).
21. A. Horeau, A. Nouaille and K. Mislow, Ibid., 87, 4957 (1965).
22. P. Love, R. W. Taft, Jr. and T. Wartik, Tetrahedron, 5, 116 (1959).
23. E. S. Lewis and C. M. Coppinger, J. Am. Chem. Soc., 76, 4495 (1954).
24. V. J. Shiner, Jr. and C. J. Verbanic, Ibid., 79, 373 (1957).
25. E. S. Lewis, R. R. Johnson and G. M. Coppinger, Ibid., 81, 3140 (1959).
26. V. J. Shiner, Jr. and G. S. Kriz, Jr., Ibid., 86, 2643 (1964).
27. V. J. Shiner, Jr. and J. S. Humphrey, Jr., Ibid., 85, 2416 (1963).
28. V. J. Shiner, Jr., Ibid., 83, 240 (1961).
29. R. L. Shone, Ph.D. Thesis, Michigan State University, 1965.
30. S. E. Scheppele, Ph.D. Thesis, Michigan State University, 1964.
31. B. L. Murr, Jr., Ph.D. Thesis, Indiana Univ., 1961.
32. C. G. Papaioannau, Ph.D. Thesis, Michigan State University, 1967.
33. G. Jones and D. M. Bollinger, J. Am. Chem. Soc., 57, 280 (1935).
34. J. B. Conant and W. R. Kirner, J. Am. Chem. Soc., 46, 245 (1924).
35. International Critical Tables, Edited by E. W. Washburn, McGraw-Hill Book Co., New York, 1928, Vol. 3, p. 33.
36. Handbook of Chemistry and Physics, Forty Second Edition, The Chemical Rubber Publishing Co., Cleveland, Ohio, p. 2142.
37. Reference 35, p. 112.
38. L. S. Bartell, J. Chem. Phys., 32, 827 (1960).

39. R. A. Scott and H. A. Scheraga, Ibid., 42, 2209 (1965).
40. J. B. Hendrickson, J. Am. Chem. Soc., 83, 4537 (1961).
41. Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, J. Chem. Phys., 21, 1927 (1953).
42. K. M. Sinnott, Ibid., 34, 851 (1961).
43. F. P. Boer, J. Am. Chem. Soc., 88, 1572 (1966).
44. J. Trotter, Acta Cryst., 13, 732 (1960).
45. M. L. Bender and M. S. Feng, J. Am. Chem. Soc., 82, 6318 (1960).
46. E. A. Halevi and Z. Margolin, Proc. Chem. Soc. (London), 1964, 174.
47. C. G. Papioannou, Private Communication.
48. M. B. Janeson and B. R. Penfold, J. Chem. Soc., 528 (1965).
49. J. M. O'Gorman, W. Shand and V. Schomaker, J. Am. Chem. Soc., 72, 4222 (1950).
50. S. Geller and J. L. Hoard, Acta Cryst., 4, 399 (1951).
51. B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, J. Mol. Spec., 2, 361 (1966).
52. K. Hedberg and V. Schomaker, J. Am. Chem. Soc., 72, 1482 (1951).

APPENDIX

Structure of 1,8-Disubstituted Naphthalene Compounds

Three different basic structures were used for the three types of substituents (hydrogen, methyl and tertiary butyl) in the 8-position. The structures of the 8-methyl substituted compounds were taken to conform with the known structure of 3-bromo-1,8-dimethylnaphthalene (48). The structures of the 8-hydrogen and 8-t-butyl substituted naphthalenes were based on reasonable estimates. In order to simplify the determination of the interatomic distances, R and X in XIX were assumed to be coplanar with the naphthalene ring.

XIX

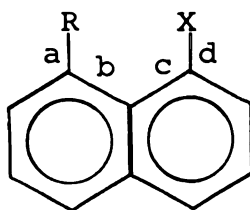


Table 16. Structural parameters of the naphthalene ring
and of R for 8-R-1-X-naphthalenes

Bond Length Å		Bond Angle	
1-X-Naphthalene (XIX, R = H)			
a	1.08	ab,cd	121°
b,c	1.42	bc	122°
8-Methyl-1-X-naphthalene (XIX, R = CH ₃)			
a	1.52	ab,cd	123.5°
b,c	1.43	bc	126.8°
8- <u>t</u> -butyl-1-X-naphthalene (XIX, R = C(CH ₃) ₃)			
a	1.52	ab,cd	125°
b,c	1.43	bc	128°
C-C	1.53	C-C-C	111°
C-H	1.10	C-C-H	111°

Table 17. Structural parameters of X for 8-R-1-X-naphthalenes

R	X	Bond	Bond Length (Å)	Bonds	Bond Angle
H, CH ₃ , C(CH ₃) ₃	CH ₂ Cl	C-C	1.52	C-C-H	109.5°
		C-H	1.10	C-C-Cl	109.5°
		C-Cl	1.78		
H, CH ₃ , C(CH ₃) ₃	CH ₂ +	C-C	1.52	C-C-H	120°
		C-H	1.10		
H, CH ₃	COCl	C-C	1.48	C-C-O	120°
		C-O	1.22	C-C-Cl	120°
		C-Cl	1.72		
C(CH ₃) ₃	COCl	C-C	1.48	C-C-O	126°
		C-O	1.22	C-C-Cl	114°
		C-Cl	1.72		
H, CH ₃ , C(CH ₃) ₃	O=C +	C-C	1.48	C-C-O	180°
		C-O	1.22		
H, CH ₃	CO ₂ Me	C-O	1.48	C-C=O	120°
		C=O	1.22	C-C-O	120°
		C-O	1.36		
H, CH ₃	COH(OMe)(O ⁻)	C-C	1.52	C-C-O	109.5°
		C-O	1.42		

Structures of Other Compounds

The structure used for the t-butyl chloride was the same as that used by Bartell (11). The structure of acetyl chloride has been determined by microwave spectroscopy (42) and the structure of the acetyl cation as the antimony-hexafluoride salt has been determined by X-ray crystallography (43). The structure of ethyl acetate was taken to be the same as the structure determined for methyl acetate (49). The structures of the boron trifluoride and diborane adducts of 2,6-dimethylpyridine were estimated by using bond lengths and angles similar to those of trimethylamine boron trifluoride (50), pyridine (51), and diborane (52).

Table 18. Structural parameters of other compounds for which isotope effects were calculated

Compound	Bond	Bond Length (Å)	Bonds	Bond Angle
$C(CH_3)_3Cl$	C-C	1.54	C-C-C	109.5°
	C-H	1.10	C-C-H	109.5°
	C-Cl	1.80		
$C(CH_3)_3 +$	C-C	1.54	C-C-C	120°
	C-H	1.10	C-C-H	109.5°
CH_3COCl	C-C	1.499	C-C-H	110.35°
	C-H	1.083	C-C-O	127.083°
	C-O	1.192	C-C-Cl	112.65°
	C-Cl	1.789		
$+ CH_3C=O$	C-C	1.38	C-C-H	110.35°
	C-H	1.083	C-C-O	180°
	C-O	1.15		
CH_3CO_2Et	C-C	1.51	C-C-H	110.3°
	C-H	1.083	C-C=O	122°
	C-O	1.36		
$CH_3C(OH)(Et)(O^-)$	C-C	1.54	C-C-H	110.3°
	C-H	1.083	C-C-O	109.5°
	C-O	1.42		
$C-CH_2Cl$	C-C	1.53	C-C-H	109.5°
	C-H	1.10	C-C-Cl	109.5°
	C-Cl	1.78		
$C-CH_2 +$	C-C	1.53	C-C-H	120°
	C-H	1.10		
$(CH_3)_2CH_3N:BH_3$	B-H	1.19	N-B-H	112°
$(CH_3)_2CH_3N:BF_3$	B-F	1.38	N-B-F	112°
	B-N	1.58	C-N-B	121.6°
	C-N	1.34	C-C-N	118°
	C-C	1.51	C-C-H	110°
	C-H	1.10		

Table 19. Values of ℓ_m and ℓ_t of 8-R-1-X-naphthalenes

R	X	Interaction	$\ell_m(\text{\AA})$	$\ell_t(\text{\AA})$
D	CH ₂ Cl	H--H	0.10	0.20
D	CH ₂ Cl	H--Cl	0.10	0.18
CD ₃	CH ₂ Cl	H--H	0.10	0.19
C ₄ D ₉	CH ₂ Cl	H--H	0.10	0.23
C ₄ D ₉	CH ₂ Cl	H--Cl	0.10	0.18
D	COCl	H--O	0.10	0.15
D	COCl	H--Cl	0.10	0.15
CD ₃	COCl	H--O	0.09	0.16
CD ₃	COCl	H--Cl	0.09	0.16
CD ₃	COCl	H--C	0.10	0.14
C ₄ D ₉	COCl	H--O	0.10	0.18
D	CO ₂ CH ₃	H--O	0.10	0.15
CD ₃	CO ₂ CH ₃	H--O	0.09	0.16
CD ₃	CO ₂ CH ₃	H--C	0.10	0.14

Table 20. Values of ℓ_m and ℓ_t for other compounds

Compound	Interaction	$\ell_m(\text{\AA})$	$\ell_t(\text{\AA})$
$(\text{CD}_3)_3\text{CCl}$	H--H	0.13	0.23
	H--Cl	0.10	0.18
	H--C	0.10	0.18
CH_3COCl	H--O	0.10	0.16
	H--Cl	0.10	0.16
	H--C	0.10	0.10
$\text{CD}_3\text{CO}_2\text{C}_2\text{H}_5$	H--O	0.10	0.16
$\text{C-CD}_2\text{Cl}$	H--H	0.135	0.135
	H--Cl	0.104	0.104
	H--C	0.086	0.086
$(\text{CD}_3)_2\text{CH}_2\text{N:BH}_3$	H--H	0.10	0.19
	H--B	0.10	0.14
$(\text{CD}_3)_2\text{CH}_2\text{N:BF}_3$	H--F	0.10	0.16
	H--C	0.10	0.14
$\text{C}_6\text{H}_4\text{BrC}_6\text{H}_4\text{Br}$	H--Br	0.10	0.16

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