Tetrahedron, 1963, Vol. 19, pp. 2009 to 2023. Pergamon Press Ltd. Printed in Northern Ireland

THE KINETIC ISOTOPE EFFECT IN THE PHOTO-CHLORINATION OF METHANE[1]

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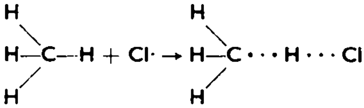
(*Received* 9 *April* 1963, *in revised form* 28 *May* 1963)

Abstract—The kinetic isotope effect for the photochemically initiated chlorination of methane-d_1 has been determined. The value is $k_H/k_D = 12{\cdot}1$ at 0°C., and the variation with temperature is given by $k_H/k_D = 1{\cdot}09 \exp(1300/RT)$. The results are considered in terms of a semiempirical potential energy surface, and the general subject of the magnitudes of primary kinetic isotope effects is discussed.

INTRODUCTION

FOR some time, we have been interested in the magnitude of the kinetic hydrogen isotope effect, and with its variation as a function of the nature of the reagent used, and of structural changes in the organic reactant.[3] As a result of recent work[4] the importance of a vibrational assignment for the activated complex has been generally recognized. It is the purpose of this paper to consider the kinetic isotope effect for the halogenation of some hydrocarbons.

The simplest case is the halogenation of methane. If we consider the process leading to the activated complex we see that there are three vibrations of methane



which need be considered, a carbon–hydrogen stretching mode and a degenerate carbon–hydrogen bending mode (one in the plane of the paper and the other perpendicular to the paper.[5] In the activated complex, there are three additional vibrations, resulting from the loss of the three translational degrees of freedom by

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[1] This work was supported by an A. P. Sloan Foundation Fellowship and by the U.S. Atomic Energy Commission.

At the time of submission of this manuscript, there appeared a paper by G. Chiltz, R. Eckling, P. Goldfinger, G. Huybrechts, H. S. Johnston, L. Meyers and G. Verbeke, *J. Chem. Phys.*, **38**. 1053 (1963) on the intermolecular isotope effect for the chlorination of mixtures of CH^4 and CD^4, The values obtained are very close to the values reported herein which refer to the intramolecular isotope effect.

[2] Taken from part of a thesis submitted by E.L.M. to the University of Washington in partial fulfillment of the requirements for the Ph.D. degree, 1961.

[3] K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.*, **80**, 3033 (1958); K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

[4] (a) J. Bigeleisen and M. Wolfsberg in *Advances in Chemical Physics*, Vol. I, p. 1. Interscience, New York (1958).

(b) H. S. Johnston in *Advances in Chemical Physics*, Vol. III, p. 131. Interscience, New York (1961).

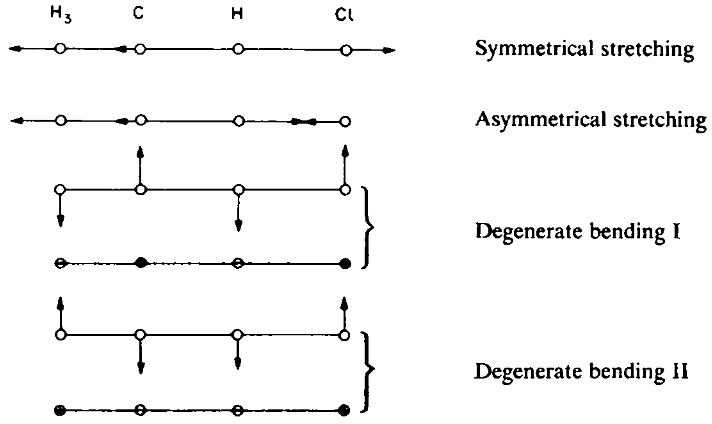
(c) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(d) L. Melander, *Isotope Effects on Reaction Rates*, pp. 24–32. Ronald Press, New York (1960).

[5] The vibrations in methane are of course coupled, but to a low order of approximation, we may speak about these three localized vibrations.

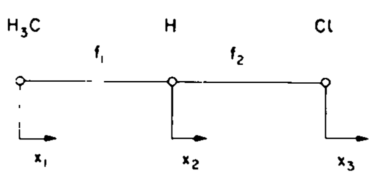
the chlorine. Two of these will be stretching frequencies, and four will be bending frequencies.

It is convenient to represent the activated complex as a four center system in which we consider the methyl hydrogens as an atom of mass three.[4b] The C–H_3 stretching force constant will be relatively large, and the C–H_3 stretching vibrations may be assumed to be relatively independent of the other vibrations. The vibrational modes will then be:



The bending force constants in the activated complex will be smaller than that in the reactant. However, since there are four bending modes in the activated complex whereas there are only two in the reactant, one might expect these zero-point energy contributions in the reactant and activated complex to approximately cancel. Thus for a qualitive argument, one need only consider the two stretching modes.

The asymmetrical stretching mode leads to product formation and degenerates to a translational mode. Consequently, there is no zero-point energy contribution associated with this mode. This is, however, not the case for the symmetrical mode. Remembering that the C–H_3 stretching force constant is usually high with respect to the other stretching force constants in the activated complex, the activated complex may be represented by



where the CH_3–H stretching force constant is f_1, the H–Cl force constant is f_2, and the displacements x_1, x_2, x_3, are from the equilibrium distances. There will also be an interaction constant (f_{12}) between CH_3 and Cl which serves to make the activated complex unstable with respect to the products or the reactants. The potential energy will be given by

$$V = -\tfrac{1}{2}f_1(x_1 - x_2)^2 - \tfrac{1}{2}f_2(x_2 - x_3)^2 + f_{12}(x_1 - x_2)(x_2 - x_3) \tag{1}$$

where the zero of energy is that of the activated complex.

Consider two reactions which have the potential energy surfaces shown in Figs. 1 and 2. The values of f_1 and f_2 may be determined by drawing lines parallel to the axes through the activated complex. One line corresponds to a change in $(x_1 - x_2)$ with $(x_2 - x_3)$ equal to zero, and gives f_1. Similarly the other gives f_2. For the case shown in Fig. 1, $f_1 \simeq f_2$. If the masses of the particles at the ends of the three particle system are approximately equal, this will lead to no motion of the hydrogen (or deuterium) in the symmetrical stretching mode of the activated complex. Thus the frequency of this vibration will not be affected by deuterium substitution and there will be no zero-point energy contribution in the activated complex. This is a case which should give a maximum isotope effect for the full zero-point energy difference of the ground state vibrational mode of the C–H and C–D bonds will contribute to the rate difference.

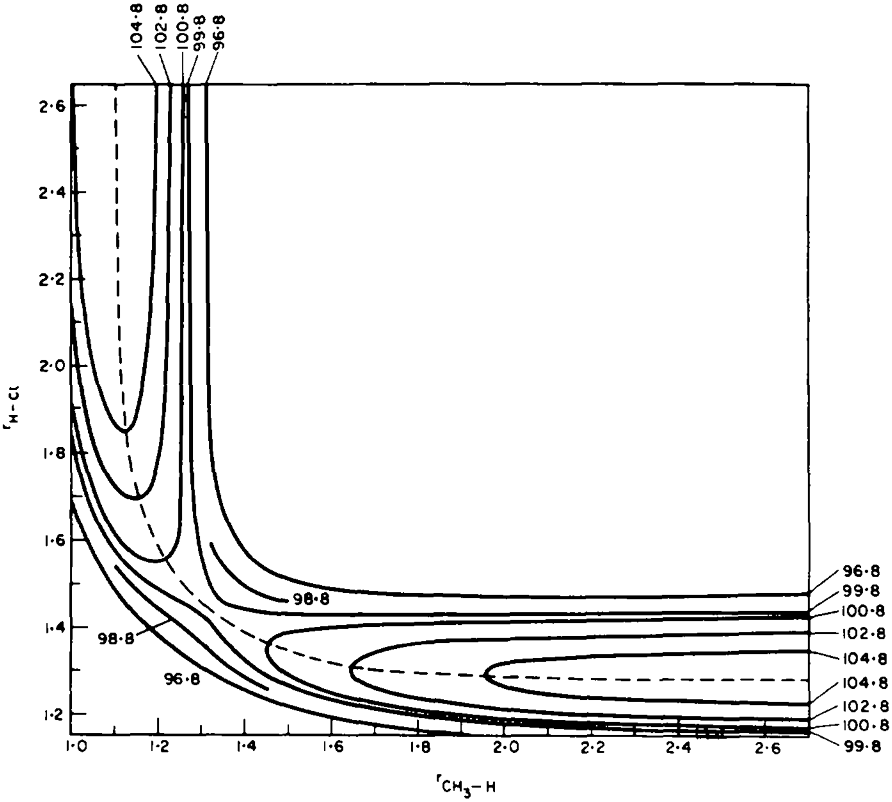


Fig. 1. Potential energy contours for the reaction of methane with chlorine atoms.

Figure 2 on the other hand represents a case in which $f_1 > f_2$, and under these conditions, the hydrogen (or deuterium) will be involved in the symmetrical stretching mode of the activated complex leading to a difference in the vibrational frequencies. The difference in zero-point energy contributions must be subtracted from that in the ground state, leading to a reduced isotope effect. In the limit where $f_1 \gg f_2$, (or $f_2 \gg f_1$) the isotope effect should be unity.

Figure 2 typifies the activated complex for the reaction of chlorine atoms with toluene for which we have observed a kinetic isotope effect $k_H/k_D = 1{\cdot}4$.[3] The potential energy surface is unsymmetrical since the dissociation energies of toluene and hydrogen chloride are quite different. A case in which chlorination should lead to a relatively symmetrical potential energy surface such as in Fig. 1 is the reaction of methane since the dissociation energies of methane and hydrogen chloride are almost equal. Therefore we have determined the kinetic isotope effect for the photochemically initiated chlorination of methane.

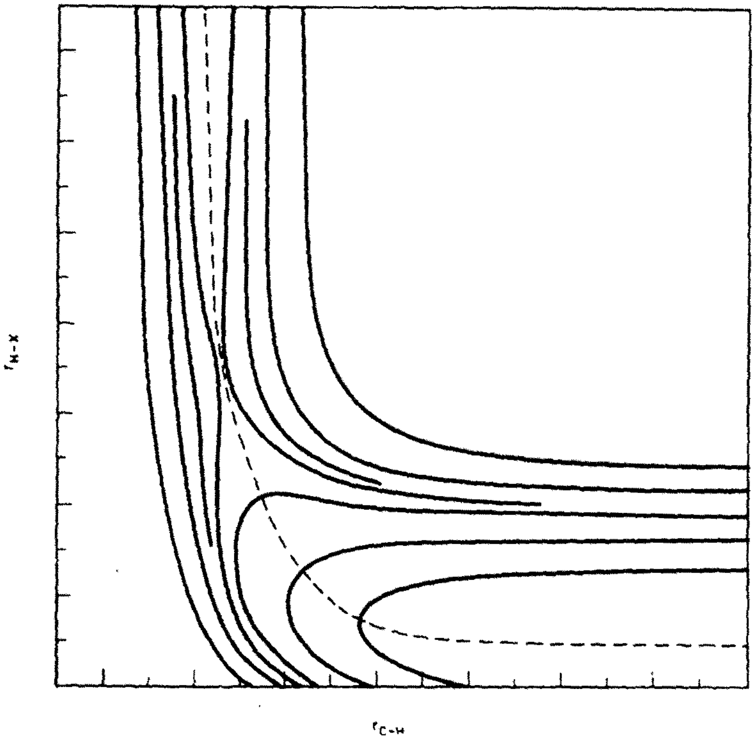


FIG. 2. Potential energy contours for a reaction for which $f_1 \gg f_2$.

RESULTS

Two different isotope effect may be measured in the chlorination of methane, the intramolecular isotope effect

$$Cl_2 + CH_2D_2 \begin{array}{l} \xrightarrow{k_H} CHD_2Cl + HCl \\ \xrightarrow[k_D]{} CH_2DCl + DCl \end{array}$$

and the intermolecular isotope effect

$$Cl_2 + CH_4 \xrightarrow{k_H} CH_3Cl + HCl$$

$$Cl_2 + CD_4 \xrightarrow{k_D} CD_3Cl + DCl$$

In both cases, there will be a secondary isotope effect to contend with, but fortunately it appears to be small for this type of reaction.[3] It will be less important with the intramolecular isotope effect as written above,[6] and the latter is experimentally the more easily measured since it is requires only one organic reactant.

The chlorination of methane presents one special problem. It is known that methyl chloride reacts with chlorine at a rate considerably higher than that for methane.[7] Thus, if the chlorination of methane-d_2 were carried to a reasonably high conversion, a considerable amount of methyl chloride would be further chlorinated. Since there would be an isotope effect associated with the latter reaction, the apparent isotope effect for the first step (based on the product ratio) would be incorrect, and in fact, would be too high.

In order to obtain the isotope effect for the first step, it seemed advisable to carry out the chlorination to several different and small degrees of completion, and then extrapolate back to zero conversion. We did not wish to make an arbitrary extrapolation back to the origin, and therefore we proceeded as follows.

A set of kinetic equations representing the reaction system may be written. If one applies the steady state approximation to eliminate the concentration of chlorine atoms and of organic radicals, the equations are

$$\begin{aligned}
\frac{d[CH_2D_2]}{dt} &= -(2AKH + 2AKD)[CH_2D_2][Cl_2] \\
\frac{d[CHD_2Cl]}{dt} &= 2AKH[CH_2D_2][Cl_2] - (2BKD + BKH)[CHD_2Cl][Cl_2] \\
\frac{d[CH_2DCl]}{dt} &= 2AKD[CH_2D_2][Cl_2] + 3AKH[CH_3D][Cl_2] \\
&\quad - (2BKH + BKD)[CH_2DCl][Cl_2] \\
\frac{d[CH_3D]}{dt} &= -(3AKH + AKD)[CH_3D][Cl_2] \\
\frac{d[CH_3Cl]}{dt} &= -3BKH[CH_3Cl][Cl_2] + AKD[CH_3D][Cl_2] \\
\frac{d[CHDCl_2]}{dt} &= 2BKD[CHD_2Cl][Cl_2] + 2BKH[CH_2DCl][Cl_2] \\
&\quad - (CKH + CKD)[CHDCl_2][Cl_2] \\
\frac{d[CD_2Cl_2]}{dt} &= BKH[CHD_2Cl][Cl_2] - 2CKD[CD_2Cl_2][Cl_2] \\
\frac{d[CH_2Cl_2]}{dt} &= 3BKH[CH_3Cl][Cl_2] + BKD[CH_2DCl][Cl_2] \\
&\quad - 2CKH[CH_2Cl_2][Cl_2] \\
\frac{d[CDCl_3]}{dt} &= 2CKD[CD_2Cl_2][Cl_2] + CKH[CHCDl_2][Cl_2] \\
&\quad - DKD[CDCl_3][Cl_2]
\end{aligned}$$

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[6] One could, of course, avoid the secondary isotope effect for the intermolecular isotope effect by measuring the ratio of the rates of hydrogen abstraction from methane and deuterium abstraction from methane-d_1. This is, however, a more difficult ratio to obtain experimentally.

[7] H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *J. Amer. Chem. Soc.*, 77, 2629 (1955).

$$\frac{d[CHCl_3]}{dt} = 2CKH[CH_2Cl_2][Cl_2] + CKD[CHDCl_2][Cl_2] - DKH[CHCl_3][Cl_2]$$

$$\frac{d[CCl_4]}{dt} = DKD[CDCl_3][Cl_2] + DKH[CHCl_3][Cl_2]$$

$$\begin{aligned}\frac{d[Cl_2]}{dt} = &-(2AKH[CH_2D_2] + 2AKD[CH_2D_2] + 2BCD[CHD_2Cl]\\ &+ BKH[CHD_2Cl] + 2BKH[CH_2DCl] + BKD[CH_2DCl]\\ &+ 3AKH[CH_3D] + AKD[CH_3D] + 3BKH[CH_3Cl]\\ &+ CKH[CHDCl_2] + CKD[CHDCl_2] + 2CKD[CD_2Cl_2]\\ &+ 2CKH[CH_2Cl_2] + DKD[CDCl_3] + DKH[CHCl_3])[Cl_2]\end{aligned}$$

These equations also include the effect of the small amount of methane-d_1 present in the methane-d_2, and of the polychlorination steps. The rate constants AKH and AKD refer to the chlorination of a C–H and a C–D bond in methane-d_2; BKH and BKD are the corresponding constants for the chlorination of methyl chloride; and CKH and CKD refer to methylene chloride; and DKH and DKD refer to the chlorination of chloroform and chloroform-d.

If one had values for the eight rate constants, the series of differential equations could be solved by numerical integration using, for example, the fourth-order Runge–Kutta method.[8] By carrying the integration to five or more half-lives, the final concentrations of each species could be determined for any given initial ratio of reactants.

This procedure was first checked using ordinary methane and the kinetic data given in the literature (Table 1). Using a methane to chlorine ratio of 19·85:1, and allowing the reaction to proceed at 0°, the ratio of methyl chloride to dichloromethane was found to be 6·7. The use of the data in Table 1 gave a ratio of 8·4. Dropping the value of E_a for the chlorination of methyl chloride to 3·25 and 3·10 kcal/mole decreased the ratio to 6·4 and 5·0 respectively. The observed and calculated amounts of chloroform and of carbon tetrachloride were negligible.

TABLE 1. KINETIC DATA FOR THE CHLORINATION OF METHANE AND OF METHYL CHLORIDES[9]

Reaction	E_a	log A
$CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$	3·9	10·4
$CH_3Cl + Cl\cdot \rightarrow CH_2Cl\cdot + HCl$	3·4 ± 0·15[a]	10·7
$CH_2Cl_2 + Cl\cdot \rightarrow CHCl_2\cdot + HCl$	6·2	12·0
$CHCl_3 + Cl\cdot \rightarrow CCl_3\cdot + HCl$	6·5	11·6

[a] Based on E_a for CH_4 = 3·9

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[8] H. Margenau and G. Murphy, *The Mathematics of Chemistry and Physics*, p. 486. Van Nostrand, Princeton (1943).

[9] P. Goldfinger, *J. chim. Phys.*, **55**, 234 (1958).

The same procedure was applied to the experimental data for the chlorination of methane-d_2. It was assumed that the secondary isotope effect would be negligible, and the rate constants for reaction at hydrogen were taken as the same as for the undeuterated compounds. The values of AKD and BKD were varied so as to give a good fit to the experimental data. It was found that the data could be fit quite well at all temperatures when E_a for the chlorination of methyl chloride was taken as 3·1 kcal/mole.[10] The effect of changes in the rate constants on the shape of the curves is shown in Fig. 3, and a comparison of the experimental data with the calculated lines is shown in Fig. 4.

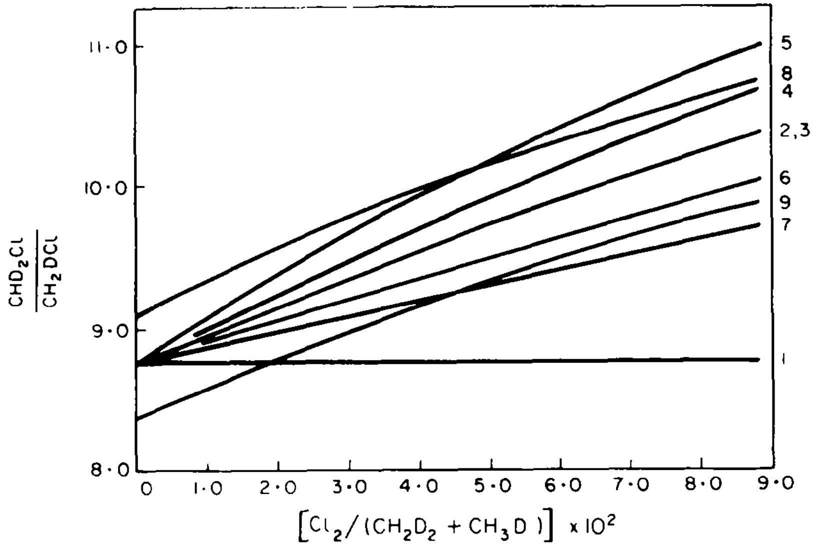

Fig. 3. Effect of changes in rate constants on the shape of the curve relating final isotopic composition of the methyl chlorides with changes in reactant ratio. The rate constants used were:

Curve	AKH	AKD	BKH	BKD	CKH	CKD	DKH	DKD
1	0·255	0·0177	3·33	3·33	0·331	0·331	0·088	0·088
2	0·255	0·0177	3·33	0·385	0·331	0·331	0·088	0·088
3	0·255	0·0177	3·33	0·385	0·000	0·000	0·000	0·000
4	0·255	0·0177	3·33	0·000	0·331	0·331	0·088	0·088
5	0·255	0·0177	5·00	0·625	0·331	0·331	0·088	0·088
6	0·255	0·0177	2·47	0·247	0·331	0·331	0·088	0·088
7	0·255	0·0177	1·83	0·214	0·331	0·331	0·088	0·088
8	0·255	0·0166	3·33	0·385	0·331	0·331	0·088	0·088
9	0·255	0·0190	3·33	0·385	0·331	0·331	0·088	0·088

The isotope effects are now simply given as the ratio of AKH/AKD, and have the values 14·4 at −23°, 12·1 at 0°, 8·2 at 52° and 7·1 at 71°. An Arrhenius plot of the data (Fig. 5) gives 1300 cal/mole as the difference in activation energy between hydrogen and deuterium abstraction, and 1·09 as the ratio of the A factors. The largest source of error in this study lies in the determination of the amount of

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[10] This slightly lower value may be necessitated by the neglect of the secondary isotope effect. The full details of the calculations and the comparisons with the various product ratios are given in the thesis of E. L. M. and will be available through University Microfilms.

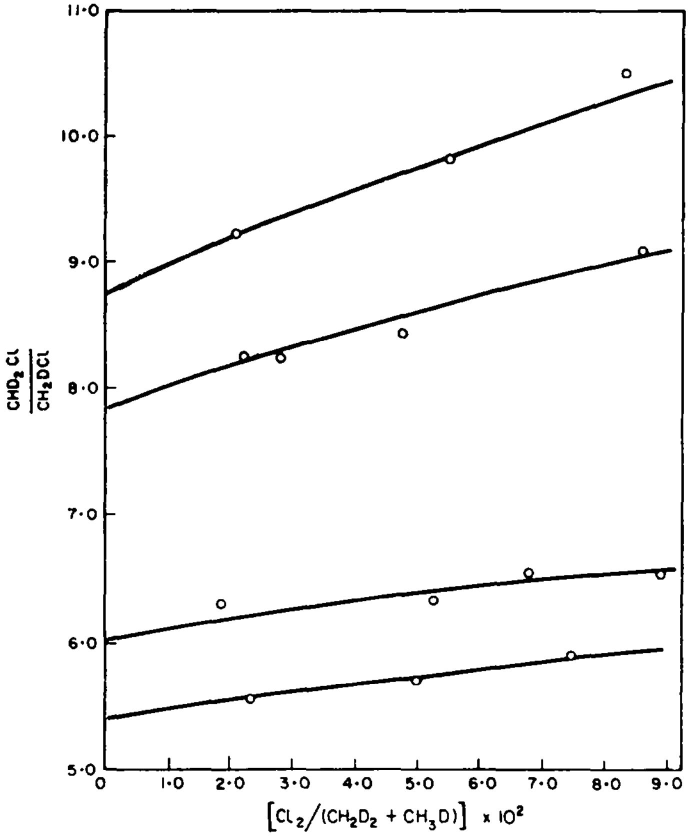


FIG. 4. A comparison of the experimental data (circles) with the calculated curves.

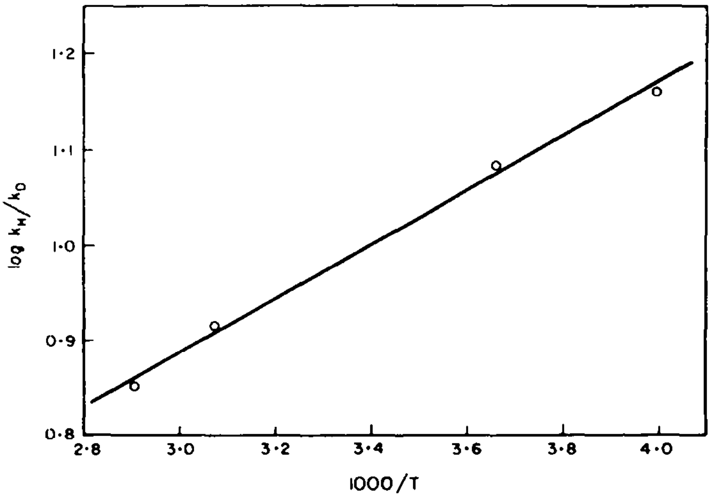


FIG. 5. Plot for obtaining the difference in activation energy between the reaction of methane and of methane-d_1 with chlorine atoms.

methane-d_1 present in the methane-d_2. This was determined mass spectrometrically to be 2·9 + 0·4%.[11] Using the extreme limits, the difference in activation energy is respectively 1230 and 1400 kcal/mole, and the ratio of A factors is 1·18 and 0·97.

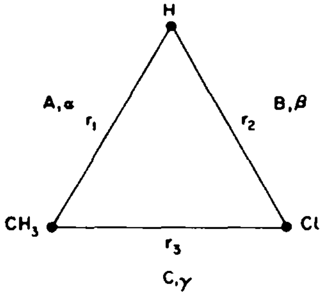
DISCUSSION

We now wish to calculate the kinetic isotope effect based on a reasonable model and to compare this with the observed value. In order to do this, it is first necessary to obtain an approximate potential energy surface for the reaction. This may be done by the entirely empirical procedure of Johnston,[4b] or by the semi-empirical method of Sato.[12] In order to be able to make an estimate of the bending constants, we have chosen to use the latter method.

The energy of an activated complex may be estimated as a function of the internuclear distances using the London three particle approximation.[13]

$$V = \left(\frac{1}{1+s^2}\right)(A + B + C - \{\tfrac{1}{2}[(\alpha-\beta)^2 + (\alpha-\gamma)^2 + (\beta-\gamma)^2]\}^{1/2}) \tag{2}$$

where A, B, and C are the Coulombic parts of the bond energy of methane, hydrogen chloride and methyl chloride respectively, and α, β, and γ are the corresponding exchange terms, and s which is required in the Sato treatment is an average value of the overlap integral.



The bond energy for any one of the three component molecules of the three atom system may be estimated as a function of bond length using the Morse equation[14]

$$V_{\text{bonding}} = D_0[(1 - e^{-a(r-r_e)})^2 - 1]$$

and the corresponding energy for the antibonding state may be estimated from Sato's equation[12]

$$V_{\text{antibonding}} = \frac{D_0}{2}[(1 + e^{-a(r-r_e)})^2 - 1]$$

In these expressions, D_0 is the bond dissociation energy using the bottom of the potential well as the origin (i.e. the observed value plus the zero-point energy for that bond), r is the distance at which the energy is to be evaluated, r_e is the

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[11] We wish to thank Dr. F. P. Lossing for making this determination.

[12] S. Sato, *J. Chem. Phys.*, **23**, 592, 2465 (1955).

[13] F. London, *Z. Elektrochem.* **35**, 552 (1929).

[14] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

equilibrium distance and α is a constant given by

$$\alpha = 1{\cdot}218 \times 10^7 \omega_0 \sqrt{(\mu/D_0)}$$

Here, ω_0 is the vibrational frequency corresponding to the minimum of the potential energy curve (usually approximated by the observed frequency and μ is the reduced mass.

Having the energies for the bonding and antibonding states, the Coulombic (Q) and exchange (L) terms may be approximated using the Heitler-London equation for a diatomic molecule[15]

$$V_{\text{bonding}} = \frac{Q + L}{1 + S^2}$$

$$V_{\text{antibonding}} = \frac{Q - L}{1 - s^2}$$

where s is the overlap integral. The value of s varies with changes in internuclear distance. However, it is only important to have a value appropriate for the distance involved in the activated complex and Sato has found that the value $s^2 = 0{\cdot}18$ fits several reactions satisfactorily. This value is of a reasonable magnitude.

Using the values of the constants given in Table 2 and making the usual assumption that the activated complex will be linear, the potential energy was evaluated at 0·1 Å intervals for a span of 2 Å, and at 0·01 Å intervals in the vicinity of the activated complex. The results are shown in the form of a contour diagram in Fig. 1. The top of the potential energy barrier has an energy of −99·8 kcal/mole, leading to a classical activation energy of 8·7 kcal/mole. This must be corrected for the zero-point energy change and the difference in heat capacity between the reactants and the activated complex, and this correction decreases the value to $\Delta H^\ddagger = 2{\cdot}8$ kcal/mole. This may be compared with the observed value $\Delta H^\ddagger = 2{\cdot}7$ kcal/mole, indicating a very good agreement. The bond lengths for the activated complex were CH_3–H 1·312 Å, and H–Cl 1·452 Å.

Table 2. Molecular constants for the methane–chlorine atom reaction

Compound	r_e	ν(cm^{-1})	α	D_0(kcal/mole)
Methane	1·090 Å	2970[a]	1·81	108·5
Hydrogen chloride	1·275	2990	1·85	106·5
Methyl chloride	1·780	732	1·72	81·0

[a] Average of symmetric and antisymmetric frequencies.

The constants f_1, f_2 and f_{12} were evaluated from 35 points in the vicinity of the activated complex using equation (1) and the method of least squares. The values thus obtained were $f_1 = 0{\cdot}711$ mdynes/Å, $f_2 = 1{\cdot}050$ and $f_{12} = 1{\cdot}470$. In order to obtain an estimate of the bending force constant, the energies of activated complexes having the bond lengths given above, but having a CH_3–Cl distance shorter than 2·60 Å, were obtained using equation (2). The bending force constants could then be evaluated using

$$\Delta V = \tfrac{1}{2} f_\phi (\Delta\phi)^2$$

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[15] W. Heitler and F. London, *Z. Phys.*, **44**, 455 (1927)

where ΔV is the change in energy from the linear activated complex and $\Delta\phi$ is the change in angle from 180°. The bending constant thus obtained was $0{\cdot}119 \times 10^{-11}$ ergs/rad.[2]

The four atom approximation is not convenient for a detailed comparison of the theoretical and experimental results when dealing with the intramolecular isotope effect. Therefore, the vibrational frequencies for the activated complex were obtained using the full six atom model,[16] assuming the force constants in the methyl group were unchanged from those in methane. The results are presented in Table 3. It may be seen that the symmetrical stretching frequency has only a very small dependence on isotopic substitution.

The absolute rate theory gives the rate of reaction as [17]

$$k = \kappa_{\text{obs}}\left(\frac{kT}{h}\right)\frac{Q^{\ddagger}}{Q_{\text{A}}Q_{\text{B}}}\,\mathrm{e}^{-\Delta E_0/RT}$$

TABLE 3. VIBRATIONAL FREQUENCIES[a]

Class	Type	CH_2D—D—Cl[b]	CD_2H—H—Cl[b]
A_1	Methyl CH stretching	2987	3031
A_1	Methyl CD stretching	2222	2158
A_1	H-C-H bending	1419	
A_1	H-C-D bending	1039	1120
A_1	D-C-D bending		1012
A_1	Bending Mode I	764	917
A_1	Bending Mode II	296	340
A_1	Symmetrical stretching	422	419
A_1	Asymmetrical stretching	1028 i	1433 i
A_2	Methyl C-H stretching	3069	
A_2	Methyl C-D stretching		2291
A_2	Bending Mode I	834	975
A_2	Bending Mode II	340	302
A_2	H-C-D bending	1229	1295

[a] The H-C-H angle, in which the second hydrogen is the one involved in the activated complex, was taken as 107°, and f_{bend} was $0{\cdot}28 \times 10^{-11}$ ergs/rad^2.

[b] Based on Cl^{35}.

where κ is the transmission coefficient, $Q^{\ddagger}$ is the partition function for the activated complex, Q_{A} and Q_{B} are the partition functions for the reactants, and ΔE_0 is the difference in energy between the reactants and activated complex at absolute zero. It is convenient to separate the zero-point energy terms from ΔE_0, giving

$$k_{\text{obs}} = \kappa\left(\frac{kT}{h}\right)\frac{Q^{\ddagger}}{Q_{\text{A}}Q_{\text{B}}}\prod_{i}^{3n^{\ddagger}-7}\mathrm{e}^{-\frac{1}{2}u_i}\prod_{i}^{3n-6}\mathrm{e}^{\frac{1}{2}u_i}\,\mathrm{e}^{-\Delta E_{\text{class}}/RT}$$

Here, $u_i = h\nu/kT$, and the products are taken over the $3n$–7 vibrations of the activated complex and the $3n$–6 vibrations of the reactants.

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[16] We wish to thank Dr. B. Kirtman for his assistance in obtaining the requisite F and G matrices. The latter are given in the thesis of E. L. M. The vibrational frequencies were computed using an IBM-709 computor and the bond angles, interaction constant and f_θ were varied. In all cases, these variations produced only a small change in the calculated isotope effect.

[17] S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York (1941).

The quantities ΔE_{class} and κ will be independent of isotopic substitution. For the intramolecular isotope effect, the reactants are the same for k_H and for k_D and the terms referring to the reactants will be the same. Thus, writing the above expression for both k_H and k_D and dividing, one obtains

$$k_H/k_D = \frac{Q_H^\ddagger}{Q_D^\ddagger} \prod_i^{3n^\ddagger-7} \frac{e^{-\frac{1}{2}u_i(H)}}{e^{-\frac{1}{2}u_i(D)}}$$

The two partition coefficients may be expressed as the products of the partition functions for translation, rotation and vibration

$$\frac{Q_H^\ddagger}{Q_D^\ddagger} = \frac{(Q_{tr}^\ddagger Q_r^\ddagger Q_v^\ddagger)_H}{(Q_{tr}^\ddagger Q_r^\ddagger Q_v^\ddagger)_D} = \left(\frac{M_H^\ddagger}{M_D^\ddagger}\right)^{3/2} \frac{(I_A^\ddagger I_B^\ddagger I_C^\ddagger)_H{}^{1/2}}{(I_A^\ddagger I_B^\ddagger I_C^\ddagger)_D{}^{1/2}} \prod_i^{3n^\ddagger-7} \frac{1-e^{-u_i(D)}}{1-e^{-u_i(H)}}$$

Here, M is the mass of the activated complex, and I_A, I_B, and I_C are the three principal moments of inertia. However, the masses of the two activated complexes will be the same, and will cancel. The isotope effect may then be written[18]

$$k_H/k_D = \frac{(I_A^\ddagger I_B^\ddagger I_C^\ddagger)_H{}^{1/2}}{(I_A^\ddagger I_B^\ddagger I_C^\ddagger)_D{}^{1/2}} \prod_i^{3n^\ddagger-7} \frac{(e^{-\frac{1}{2}u_i(H)})(1-e^{-u_i(D)})}{(e^{-\frac{1}{2}u_i(D)})(1-e^{-u_i(H)})}$$

Using the bond distances calculated above, the square root of the ratio of the moments of inertia was found to be 1·18. The expression may now be evaluated as a function of temperature using the vibrational frequencies in Table 2. This gives the data in Table 4. The calculated values may be represented by

$$k_H/k_D = 1{\cdot}15\, e^{1080/RT}$$

The agreement with the observed values

$$k_H/k_D = 1{\cdot}098\, e^{1300/RT}$$

may be considered to be good. The results indicate that tunneling through the potential energy barrier[19] is not particularly important in this reaction for the temperature range used. One would not come to this conclusion based on the shape of the barrier indicating, as has been noted previously, that the Sato procedure exaggerates the curvature of the potential energy surface in the vicinity of the activated complex and leads to too high a value of the interaction constant, f_{12}.[19] A decrease in the interaction constant will, in this case, have no effect on the ratio of the symmetrical stretching frequencies for the two activated complexes. Similarly,

TABLE 4. CALCULATED ISOTOPE EFFECTS

Temp (°C)	k_H/k_D (obs)	k_H/k_D (calc)
−23	14·4	10·4
0	12·1	8·6
25		7·2
52	8·2	6·2
71	7·1	5·6

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[18] L. Melander, *Isotope Effects on Reaction Rates*, p. 15. Ronald Press, New York (1960).

[19] Cf. J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **23**, 1535 (1955).

proportional changes in f_1 or f_2 will have no effect. The only force constant whose change leads to a change in the calculated kinetic isotope effect is f_ϕ. A decrease in this force constant, which might be necessitated by a decrease in f_{12}, would result in a larger calculated isotope effect which would be in better agreement with the observed values. It can be seen that although the model used leads to a satisfactory prediction of the isotope effect, the geometry of the activated complex is not defined by the isotope effect.

THE MAGNITUDE OF KINETIC HYDROGEN ISOTOPE EFFECTS

The present observation that the kinetic hydrogen isotope effect in the chlorination of methane is large, in contrast to the chlorination of toluene, emphasizes the importance of considering the symmetry of the activated complex[20] in discussing the magnitude of the isotope effect. The activation energy for the reaction has no large direct influence on the isotope effect, for symmetrical activated complexes may be found which have energies only slightly greater than that of the reactants (as in the present case), and which have energies considerably higher than that of the reactants.

It is often observed that there is a correlation between the magnitude of the kinetic isotope effect and the activation energy for a series of reactions.[3] This arises when factors which change the activation energy also change the symmetry of the activated complex. An example is the reaction of toluene, ethylbenzene and isopropylbenzene with N-bromosuccinimide for which at 77° $k_H/k_D = 4{\cdot}86$, $2{\cdot}67$ and $1{\cdot}81$ respectively.[3] In the reaction with toluene, the activated complex will be relatively symmetrical leading to the large isotope effect. This is the case because the dissociation energies of the C–H bond in toluene and of the H–Br bond in the product hydrogen bromide are approximately equal.[21] The addition of an α-methyl group decreases the C–H bond dissociation energy, and f_1 becomes greater than f_2. The change in ratio of force constants from approximately unity results in a zero-point energy difference in the symmetrical stretching mode in the activated complex and a decrease in the isotope effect. The addition of a second α-methyl group accentuates the effect.

For most reactions which have been studied, one does not know if quantum mechanical tunneling through the potential energy barrier will be important. Significant tunneling has been reported in the base catalyzed reaction of 2-carbethoxycyclopentanone with bromine,[22] and in the dehydrohalogenation of 1-bromo-2-phenylpropane.[23] Unfortunately, it is difficult to obtain precise data over a sufficiently large temperature range to permit an accurate determination of the difference in activation parameters between the labeled and unlabeled compound, and the possible test using a comparison of deuterium and tritium isotope effects has not been used. However, the limited data which are available suggest that

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[20] A symmetrical activated complex is considered as one in which the masses of the end atoms and the force constants are balanced so that the reacting hydrogen or deuterium is not involved in the symmetrical stretching vibration.

[21] The active hydrogen abstracting species appears to be a bromine atom: R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 354 (1963); G. A. Russel, C. DeBoer and K. M. Desmond, *J. Amer. Chem. Soc.*, **85**, 365 (1963).

[22] R. P. Bell, J. A. Fendley and J. R. Hulett, *Proc. Roy. Soc.* **235A**, 453 (1956).

[23] V. J. Shiner, Jr. and M. L. Smith, *J. Amer. Chem. Soc.*, **83**, 593 (1961).

near room temperature the change in preexponential factor due to tunneling approximately cancels the change in the activation energy term leading to an apparently normal isotope effect.

If one accepts the above assumption, the data which are now available clearly show that hydrogen abstraction as a proton, hydrogen atom, or hydride ion leads to a range of k_H/k_D values from very small to about seven at 25°, and sometimes to even higher values.[24,25] The data for proton and hydrogen atom abstraction have been reviewed previously,[3] and it need only be added that the isotope effect for the hydride transfer between cycloheptatriene and the di-*p*-anisylphenylmethyl cation is 5·0.[26]

As suggested by Hawthorn and Lewis,[24] the one case in which one might expect generally small isotope effects is in reactions leading to markedly non-linear activated complexes. This results from the fact that here the reaction coordinate corresponds more closely to a bending motion than to bond stretching, and the loss of a bending mode in going to the activated complex would result in an isotope effect about 3·5. The one good model for this type of reaction is hydrogen transfer in an intramolecular rearrangement. It has been found that the solvolysis of 3-methyl-2-butyl-3d-tosylate which involves a hydrogen shift gives an isotope effect $k_H/k_D = 2{\cdot}3$[27] and that the pinacol rearrangement of 1, 1, 2-triphenylethylene-1-d glycol gives an isotope effect $k_H/k_D = 2{\cdot}3$ to 3·3 depending on catalyst used.[28] These data are too limited to permit a generalization, but they are in accord with the expected value.

EXPERIMENTAL

Materials

Methane-d_2 was obtained from Merck and Co. Ltd., and was transferred to a reservoir attached to the vacuum system (see below) and degassed. Methyl-d_1 alcohol was prepared by the acid catalyzed decomposition of diazomethane in deuterium oxide,[29] and was purified by gas chromatography. Methyl-d_2 alcohol was prepared by the addition of isoamyl formate (4·46 g) to 1·0 g. of lithium aluminum deuteride in 40 ml of anhydrous diethyl carbitol, maintaining the temperature at about 60°. Then reaction mixture was heated to 75° for 3 hr, and then cooled to 0°. An excess of 2-ethoxyethanol was added, and the methyl-d_2 alcohol was removed by passing a slow stream of nitrogen through the mixture held at 100°. The methanol was collected by passing the exit nitrogen through a liquid nitrogen cooled trap. It was purified by gas chromatography. The two alcohol

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[24] An isotope effect of about seven at 25° corresponds to the loss of one stretching mode in going to the activated complex. In general, there will also be two bending modes in the reactant and four bending modes in the activated complex, but there is usually rough cancellation of zero-point energies due to bending. However, if the activated complex had the unusually weak bonding, as might be the case if Coulombic repulsion between the two end groups were important, the bending frequencies in the activated complex might be very low. The maximum isotope effect for the loss of the zero-point energy due to the stretching mode and one bending mode of the reactant would be about eighteen; and that for the loss of the stretching mode and both bending modes would be about forty-eight.

[25] M. F. Hawthorn and E. S. Lewis, *J. Amer. Chem. Soc.*, **80,** 4296 (1958), have suggested that hydride abstraction reactions should give small isotope effects.

[26] Private communication, H. J. Dauben, Jr.; cf. Ph.D. Thesis of L. McDonough, University of Washington, 1960.

[27] S. Winstein and J. Takahashi, *Tetrahedron* **2,** 316 (1958).

[28] C. J. Collins, W. T. Rainey, W. B. Smith and I. A. Kaye, *J. Amer. Chem. Soc.*, **81,** 460 (1959).

[29] A. Murry and D. L. Williams, *Organic Synthesis with Isotopes*, p. 1336. Part II, Interscience, New York (1958).

samples were converted to the chlorides by treatment with aluminium chloride[30] and were purified by gas chromatography.

Chlorination procedure

Known pressures of methane and of purified chlorine were transferred to two flasks having known volumes using a vacuum line. The pressures were determined using a diaphragm null gauge, and KEL-F grease was used on all stopcocks. In a darkened room, both the methane and chlorine were transferred to a reaction vessel which was wrapped in aluminum foil. The reaction was placed in a thermostat, and after 30 min, the aluminum foil was removed and the flask was irradiated with a mercury vapor lamp.

The mass spectrum of the reaction mixture was determined. The reaction vessel was attached to a vacuum line and cooled to −183° and the methane was distilled into a bulb containing silica gel at −193°. The mass spectrum of the reaction product was obtained. The hydrogen chloride was removed with potassium hydroxide and the methyl chloride was separated by gas chromatography. The mass spectrum of the purified methyl chloride was obtained at the ionizing voltages 8·8, 9·0, 9·4, 9·6, 9·8, 10·0, and 12·0 (30 mil slit, 35 μA ionizing current, repellers shorted. A Consolidated 21–103C mass spectrometer was used).

The relative sensitivities of the mass spectrometer to methyl chloride, methyl-d_1 chloride and methyl-d_2 chloride were determined using the synthetic samples. This permitted a calculation of the isotopic content of the product methyl chloride. The relative sensitivities of methylene dichloride and its deuterated derivatives were assumed to be the same in calculating the product composition.

All of the data, and the required calculations are contained in the Ph.D. Thesis of E.L.M., and are available through University Microfilms.

[30] J. F. Norris and B. M. Sturgis, *J. Amer. Chem. Soc.* **61**, 1413 (1939).