KINETIC ISOTOPE EFFECTS IN THE PHOTOCHLORINATION OF GASEOUS ETHYL CHLORIDE-2-d_1
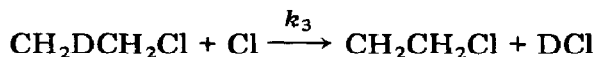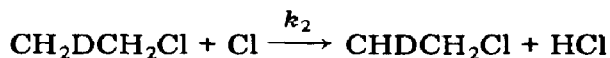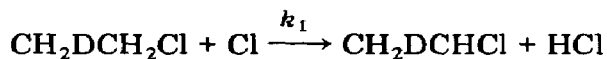
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Summary

The abstraction of hydrogen and deuterium atoms from CH_2DCH_2Cl by ground state chlorine atoms generated photochemically from chlorine has been studied at temperatures between 9 and 95 °C. The relative rates for the internal competition

$$CH_2DCH_2Cl + Cl \xrightarrow{k_1} CH_2DCHCl + HCl$$

$$CH_2DCH_2Cl + Cl \xrightarrow{k_2} CHDCH_2Cl + HCl$$

$$CH_2DCH_2Cl + Cl \xrightarrow{k_3} CH_2CH_2Cl + DCl$$

are found to conform to an Arrhenius rate law:

$$\frac{k_1}{k_2} = (1.77 \pm 0.05) \exp\left(\frac{383 \pm 14}{T}\right)$$

$$\frac{k_1}{k_3} = (5.64 \pm 0.45) \exp\left(\frac{728 \pm 26}{T}\right)$$

$$\frac{k_2}{k_3} = (3.22 \pm 0.12) \exp\left(\frac{345 \pm 12}{T}\right)$$

The moderately strong "primary" kinetic isotope effect k_2/k_3 decreases with increasing temperature from 5.51 at 280 K to 4.08 at 365 K. Neither the magnitude of the primary kinetic isotope effect nor the activation energy compares favourably with the values obtained using the bond energy–bond order method. The occurrence of a weak α secondary kinetic isotope effect,

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invariant with temperature, was established indirectly. The absolute Arrhenius factors for k_2 and k_3 were obtained by two independent calculations yielding results in satisfactory agreement with each other.

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1. Introduction

In a recent paper from this laboratory the photochlorination of gaseous ethyl chloride-1-d_1 was investigated [1]. The primary kinetic isotope effect was determined and found to be in close agreement with predictions based on the bond energy−bond order (BEBO) method developed by Johnston and Parr [2, 3]. The present study of the photochlorination of ethyl chloride-2-d_1 was a logical extension of the former work and was undertaken with the following objectives in mind: firstly, to determine accurately the primary kinetic isotope effect and the relevant absolute rate parameters; secondly, to check the usefulness of BEBO calculations further; thirdly, to complement the growing number of results of different deuterated ethyl chlorides [4, 5], in order to examine the inner self-consistency of an emerging pattern of kinetic data.

2. Experimental details

The apparatus, the light source and the experimental procedure have been described previously [4]. Photolyses were performed over the temperature range 9 - 95 °C using filtered visible light centred at 424 nm. Under the experimental conditions used the only products are 1,1- and 1,2-dichloroethanes. Analyses were performed by gas chromatography (GC) in the first instance to separate 1,1-dichloroethane from the sum of the 1,2-dichloroethanes. Coupled GC−mass spectrometry (GC−MS) was used to resolve the isotopically different 1,2-dichloroethanes.

For each dichloroethane three different parent peaks, representing the natural isotopic abundance of $^{35}Cl_2$, $^{35}Cl^{37}Cl$ and $^{37}Cl_2$ in the molecules, were observed. Since the peaks corresponding to the $^{37}Cl_2$, i.e. $m/e = 102$ for $C_2H_4Cl_2$ and $m/e = 103$ for $C_2H_3DCl_2$, were appreciably smaller, the analyses were much less accurate and these data were discarded. Thus, only four peaks were monitored: 98, 99, 100 and 101. Ideally the ratio I_{98}/I_{99} of the peak height for $m/e = 98$ to that for $m/e = 99$ should be identical with the ratio I_{100}/I_{101} of the peak height for $m/e = 100$ to that for $m/e = 101$, and both yield the contribution of the deuterated species to the total yield of 1,2-dichloroethane. However, the parent ions were always found to be accompanied by some fragment ions. Therefore, pertinent corrections, based on the cracking patterns of all four products involved, CH_3CHCl_2, CH_2DCHCl_2, CH_2ClCH_2Cl and $CHDClCH_2Cl$ (Table 1), were always introduced. For non-deuterated dichloroethanes, these fragmentation patterns were obtained using both authentic samples and the products of the photo-

TABLE 1

Mass spectral cracking patterns of normal and monodeuterated dichloroethanes[a]

	Relative peak heights for the following m/e values			
	98	99	100	101
CH_3CHCl_2	100	5.8 ± 0.6	90.1 ± 0.9	2.2 ± 0.3
CH_2ClCH_2Cl	100	3.8 ± 0.4	87.0 ± 1.0	1.8 ± 0.6
CH_2DCHCl_2	13.3 ± 0.3	100	15.5 ± 0.3	98.2 ± 0.7
$CHDClCH_2Cl$	8.1 ± 0.2	100	11.2 ± 0.4	94.8 ± 0.8

[a] The error limits are $\pm 1\sigma$.

chlorination of normal ethyl chloride under our experimental conditions. Both sets of results agreed satisfactorily, and the data shown in Table 1 represent average values. For 1,2-dichloroethane-d_1 ($CH_2ClCHDCl$) a commercial sample and that produced by the photochlorination of ethyl chloride-1-d_1 (CH_3CHDCl), and isolated by GC, were used. Again, the agreement was satisfactory. In the case of 1,1-dichloroethane-2-d_1 (CH_2DCHCl_2) a commercial sample was unavailable to us; therefore, only the compound obtained by the photochlorination of ethyl chloride-2-d_1 (CH_2DCH_2Cl) could be used.
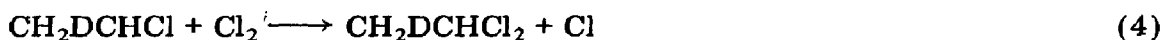
As noted previously, the fragmentation patterns determined were found to depend to some extent on the operating parameters of the mass spectrometer [1]. Thus, every series of experiments, including all the necessary calibrations, was completed under unchanged conditions. The reliability of these procedures was examined by introducing a known mixture of CH_3CH_2Cl and CH_2ClCH_2Cl (diluted with hydrogen) into the ion source. The composition of the mixture was reproduced accurately to within 1%.

Ethyl chloride-2-d_1 (Merck, Sharp and Dohme) 99% D was purified by distillation *in vacuo* (at methanol slush temperature) until the amount of the main impurity CH_3Cl decreased below the level of detection. The isotopic purity quoted by the manufacturer was confirmed by MS analyses. Normal ethyl chloride and chlorine were obtained from Matheson and purified as described previously [4].

3. Results and discussion

The photochlorination of CH_2DCH_2Cl has been studied over the range of temperatures 9 - 95 °C at total pressures of about 21 Torr. The ethyl chloride was used in about twentyfold excess over chlorine which ensures the validity of the long-chain assumption and chain termination predominantly by radical—radical combination [4]. Sufficiently low light intensities and short photolysis times were used to prevent the formation of detectable amounts of secondary photochlorination products (trichloroethanes).

Under these conditions the reaction products are formed by the propagation reactions:

$$CH_2DCH_2Cl + Cl \longrightarrow CH_2DCHCl + HCl \tag{1}$$

$$CH_2DCH_2Cl + Cl \longrightarrow CHDCH_2Cl + HCl \tag{2}$$

$$CH_2DCH_2Cl + Cl \longrightarrow CH_2CH_2Cl + DCl \tag{3}$$

$$CH_2DCHCl + Cl_2 \longrightarrow CH_2DCHCl_2 + Cl \tag{4}$$

$$CHDCH_2Cl + Cl_2 \longrightarrow CHDClCH_2Cl + Cl \tag{5}$$

$$CH_2CH_2Cl + Cl_2 \longrightarrow CH_2ClCH_2Cl + Cl \tag{6}$$

The radicals formed in reactions (1) - (3) are thermal and hence can neither dissociate nor undergo any isomerizations prior to reaction with molecular chlorine. It has been shown previously [4, 6] that, for low conversions, other side reactions, i.e. hydrogen–deuterium and/or chlorine exchange, or the abstraction of hydrogen atoms or deuterium atoms from the product chlorohydrocarbons do not play any significant role.

Reactions (1) - (3) represent an internal competition system (between α and β hydrogen atoms). For long chains, the product ratio gives the rate constant ratio for the abstraction reaction directly [4]:

$$\frac{k}{k'} = \frac{[RCl]}{[R'Cl]} \tag{7}$$

For reactions (2) and (3) the rate constant ratio k_2/k_3 yields a first approximation to the magnitude of the primary kinetic isotope effect, i.e. the effect resulting from the rupture of the C—H and C—D bonds respectively (see later). Since the task of resolving the CH_2ClCH_2Cl and $CHDClCH_2Cl$ pair could not be accomplished by GC alone, the photolytic products were subjected to GC–MS analysis. The temperature dependence of k_2/k_3 is shown in Fig. 1, where the experimental points are averages at three or four measurements. Over the range of temperatures covered in this study the results conform to an Arrhenius rate law, and the relative rate parameters, based on a least-squares treatment, are given in Table 2. The overall accuracy is affected adversely by the occurrence of a systematic error of unknown origin, which manifests itself in the slight inequality of the results obtained using I_{99}/I_{98} and I_{101}/I_{100} monitoring. However, the uncertainties in the relative Arrhenius factors are about 3.5% which is sufficient for the purpose of establishing the primary kinetic isotope effect.

To obtain the absolute Arrhenius parameters for k_2 and k_3 use was made of reaction (1) as the internal standard, for which the rate constant has recently been accurately determined [5]. To this end, the ratio $c_i/c_j = [CH_2DCHCl_2]/([CHDClCH_2Cl] + [CH_2ClCH_2Cl])$ was measured by GC as a function of reaction temperature. The plot shown in Fig. 2 is also linear and obeys the following expression:

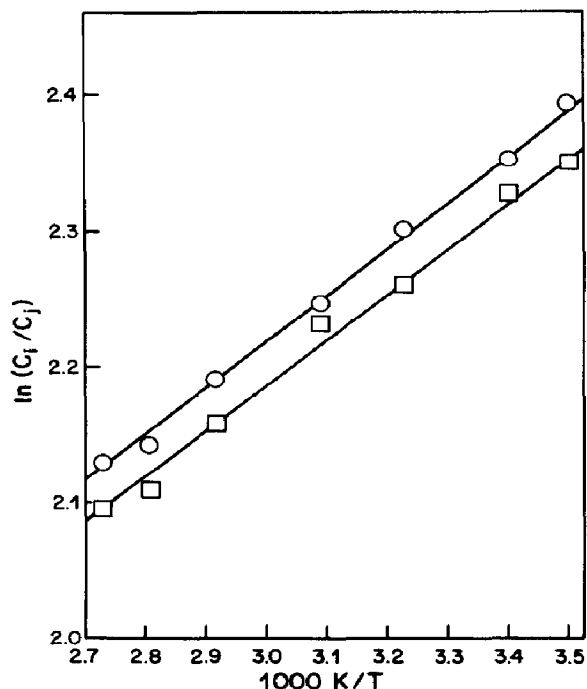$$\ln\left(\frac{k_1}{k_2 + k_3}\right) = (0.360_5 \pm 0.13) + \frac{416 \pm 4}{T} \tag{8}$$

Fig. 1. Temperature dependence of the rate ratios for internal competition (c_i/c_j = [$CHDClCH_2Cl$]/[CH_2ClCH_2Cl] in GC–MS experiments): O, I_{99}/I_{98}; □, I_{101}/I_{100}.

TABLE 2

Relative Arrhenius parameters for hydrogen and deuterium abstraction by chlorine atoms obtained from internal competition gas chromatography–mass spectrometry experiments[a]

Competitors	A_2/A_3[b]	$(E_3 - E_2)/R$ (K)	Monitoring ratio
CH_2DCH_2Cl–CH_2DCH_2Cl	3.25 ± 0.11	346 ± 11	I_{99}/I_{98}
	3.19 ± 0.10	343 ± 9	I_{101}/I_{100}
	3.22 ± 0.12	345 ± 12	I_{99}/I_{98} and I_{101}/I_{100}

[a] Stated error limits are $\pm 1\sigma$. Both precision of analyses and errors involved in the determination of correction factors for detector sensitivity are accounted for.
[b] Statistical A factor ratio (not reduced on a per atom basis).

where the stated error limits are one standard deviation and account for both the precision of experiments and the systematic errors due to uncertainties in the calibration coefficients for the GC detector sensitivity towards 1,1- and 1,2-dichloroethanes. This relative correction factor was determined previously [6] as [CH_3CHCl_2] = $(1.057 \pm 0.013) \times$ [CH_2ClCH_2Cl]. However, the small difference in the detector response towards monodeuterated 1,2-dichloroethane was ignored. The Arrhenius-like expression (8) has no simple physical meaning but is nevertheless useful in providing a numerical way of extracting the temperature dependences of k_2 and k_3. Using the relative
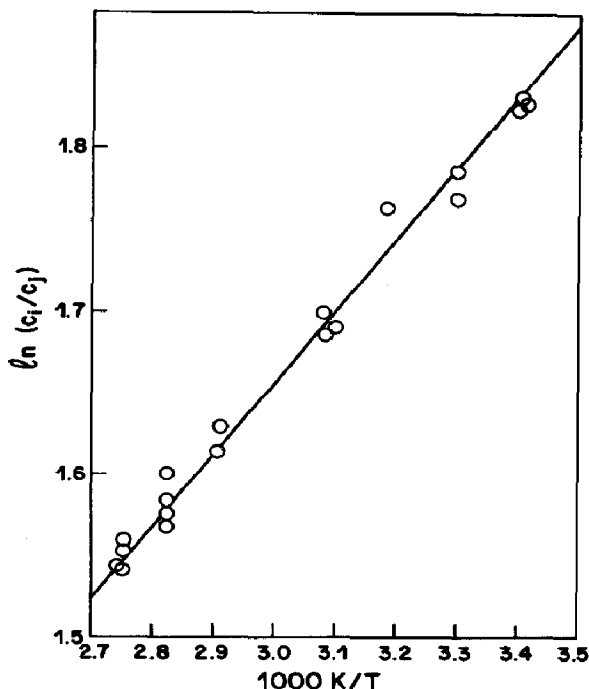
Fig. 2. Temperature dependence of the rate ratios for internal competition (c_i/c_j = [CH$_2$DCHCl$_2$]/([CH$_2$ClCH$_2$Cl] + [CHDClCH$_2$Cl])) in GC experiments; the correction factors for the flame ionization detector sensitivity are not included.

Arrhenius parameters listed in Table 2, which are based on the GC–MS analysis, numerical values of k_2/k_3 are evaluated as a function of temperature. Substitution of these data in eqn. (8) yields the temperature dependences of k_1/k_2 and k_1/k_3, which satisfy the expressions

$$\ln\left(\frac{k_1}{k_2}\right) = (0.57 \pm 0.03) + \frac{383 \pm 14}{T} \tag{9}$$

$$\ln\left(\frac{k_1}{k_3}\right) = (1.73 \pm 0.08) + \frac{728 \pm 26}{T} \tag{10}$$

The absolute Arrhenius parameters for k_2 and k_3 can now be readily evaluated since k_1 is known [5]. These results are assembled in Table 3.

It should be noted that the measured "primary" kinetic isotope effect k_2/k_3 = [CH$_2$DCH$_2$Cl]/[CH$_2$DCH$_2$Cl] hitherto considered does not, in fact, represent a pure primary effect but incorporates a contribution from the α secondary effect. These contributions can be factored out by applying an iterative procedure analogous to that recently described [5]. In the identity expression

$$\frac{k(CH_3R)}{k(CD_3R)}\left\{\frac{k(CH_2DR)}{k(CH_2DR)}\right\}^{-1} \equiv \frac{k(CH_2DR)}{k(CHD_2R)} \frac{k(CH_3R)}{k(CH_2DR)} \frac{k(CHD_2R)}{k(CD_3R)} \approx (KIE_{\alpha\,sec})^3$$

TABLE 3

Absolute Arrhenius parameters for hydrogen and deuterium atom abstraction from ethyl chlorides by chlorine atoms[a]

Reactant	A ($\times 10^{-11}$ cm^3 s^{-1})		E_a (cal mol^{-1})	Reference
	Statistical	Per available H or D atom		
CD_3CH_2Cl	1.08 ± 0.03	0.36 ± 0.01	2358 ± 9	[8]
CH_3CH_2Cl	2.13 ± 0.05	0.71 ± 0.02	1682 ± 6	[6]
CH_2DCH_2Cl	2.15 ± 0.04	1.08 ± 0.02	807 ± 7	[5]
CH_2DCH_2Cl	1.22 ± 0.04	0.61 ± 0.02	1568 ± 16	This work[b]
	1.37 ± 0.05	0.68 ± 0.03	1681 ± 13	This work[c]
CH_2DCH_2Cl	0.38 ± 0.03	0.38 ± 0.03	2254 ± 27	This work[b]
	0.39 ± 0.02	0.39 ± 0.02	2357 ± 15	This work[c]

[a] Based on the reaction $CH_4 + Cl \rightarrow CH_3 + HCl$ as primary standard; k (cm^3 s^{-1}) = $(1.65 \pm 0.32) \times 10^{-11} \exp\{-(1530 \pm 68)/T\}$ from ref. 7.
[b] Direct GC–MS determination.
[c] Indirect evaluation based on the estimates for the α effect.

where $R \equiv CH_2Cl$, $CHDCl$ and CD_2Cl, the ratios on the left-hand side have been experimentally determined, while those on the right-hand side represent three different α secondary effects which are non-separable by GC analysis. By assuming their equality, which does not seem to be an over-simplification, a geometric mean value for the α secondary kinetic isotope effect can be readily evaluated. Such a procedure, using three independent sets of GC data taken from our recent publication [8] against a set of GC–MS data from this work (Table 4), yields the values shown in Table 5. As expected, there are some differences since the abstraction of deuterium atoms from either the CHD_2 or the CD_3 group is affected by the isotopic composition of the adjacent chloromethyl group R. However, taking into account the limitations in accuracy and the approximation involved in the evaluative procedure, any efforts to extricate this β secondary effect would not be warranted. Nevertheless, some conclusions can be drawn. The following expression, based on the data reported in Table 5, for the α secondary kinetic isotope effect

$$KIE_{\alpha\,sec} = (1.04 \pm 0.03_5) \exp\left(-\frac{1 \pm 12}{T}\right) \qquad (12)$$

refers to the replacement of one hydrogen atom by a deuterium atom in the methyl group. Although the assessment of the magnitude of the α effect is only approximate, its very occurrence does not seem to be in doubt and the trend observed resembles that established for the β effects [5, 6]: the substitution of hydrogen by deuterium in the immediate vicinity of the hydrogen or deuterium atom being abstracted lowers the rate constant for abstraction. Numerically, in this case, the α effect is relatively small and only slightly larger than the β secondary kinetic isotope effects reported for the ethyl chloride system. In the case of two hydrogen atoms being replaced, the

TABLE 4

Mixed (primary and α secondary) kinetic isotope effects for hydrogen and deuterium abstraction by chlorine atoms

	k_i/k_j for the following temperatures			
	280 K	310 K	340 K	370 K
$CH_3CH_2Cl-CD_3CH_2Cl$ [a]	6.62 ± 0.21	5.88 ± 0.18	5.34 ± 0.16	4.92 ± 0.15
$CH_3CHDCl-CD_3CHDCl$ [a]	5.97 ± 0.16	5.27 ± 0.14	4.75 ± 0.12	4.35 ± 0.11
$CH_3CD_2Cl-CD_3CD_2Cl$ [a]	5.94 ± 0.19	5.31 ± 0.17	4.85 ± 0.15	4.49 ± 0.14
$CH_2DCH_2Cl-CH_2DCH_2Cl$ [b]	5.51 ± 0.31	4.89 ± 0.26	4.43 ± 0.23	4.08 ± 0.20

[a] GC data [8].
[b] Present GC–MS data.

TABLE 5

α secondary kinetic isotope effects for deuterium atom abstraction by chlorine atoms

	k_i/k_j for the following temperatures			
	280 K	310 K	340 K	370 K
$CHD_2CH_2Cl-CD_3CH_2Cl$	1.063	1.063	1.064	1.064
$CHD_2CHDCl-CD_3CHDCl$	1.027	1.025	1.024	1.022
$CHD_2CD_2Cl-CD_3CD_2Cl$	1.025	1.028	1.031	1.032
CHD_2R-CD_3R [a]	1.038	1.039	1.039	1.039

[a] Arithmetic average for α secondary kinetic isotope effect (any β contributions are ignored).

corresponding α effect $k(CH_2DCH_2Cl)/k(CD_3CH_2Cl)$ is expected to be larger, but probably not more than twice the reported value. Yet, even in this case the effect will be smaller than that associated with deuterium atom abstraction from the chloromethyl group [5]. Finally, the former conclusion that the α effect in $CH_3CHDCl-CH_3CD_2Cl$ is independent of temperature [5] is also confirmed by the present results, over the range of temperatures covered in these studies.

The value of $KIE_{\alpha\,sec}$ given in eqn. (12) provides a quick estimate of the rate parameters for hydrogen and deuterium abstraction in CH_2DCH_2Cl and CH_2DCH_2Cl from CH_3CH_2Cl and CD_3CH_2Cl respectively. The evaluations are included in Table 3. It is seen that the results pass the check for internal self-consistency satisfactorily. Of the two sets of absolute Arrhenius parameters shown in Table 3 those based on the direct GC–MS measurements are naturally preferred.

3.1. Bond energy–bond order calculations

In a recent paper from this laboratory the BEBO method was applied with seeming success to predict the kinetic isotope effect for the abstraction of secondary hydrogen by chlorine atoms from ethyl chloride-1-d_1 [1]. The

discrepancies between the calculated and the experimental values were of the order of 5% - 6%. However, even a superficial glance at the results presented in this work leads to the conclusion that for ethyl chloride-2-d_1 the BEBO method will be a disappointment. The details of the BEBO theory, presented comprehensively by Johnston [3], need not be repeated here. It suffices to point out that the final results of the calculations depend naturally on the input parameters used. The parameters appropriate for ethyl chloride-2-d_1 are shown in Table 6 and, for comparison, those used previously for the ethyl chloride-1-d_1 are also included. The C—H bond energies in the ethyl chlorides are estimates by Franklin and Huybrechts [9] and the difference between the primary and the secondary hydrogen atoms is 1.3 kcal mol^{-1}. Such a small difference has little impact on the value of the BEBO parameter p which plays a crucial role in the calculations. Therefore, all subsequent results for both ethyl chlorides are very similar. The potential energy V^* of activation ($V^* = 8.20$ kcal mol^{-1}) was found at $n^* = 0.50$. This value exceeds the experimental activation energy by about 6 kcal mol^{-1}, which confirms the failure of the BEBO method in predicting activation energies for this class of reactions.

TABLE 6

Input parameters for bond energy–bond order calculations

Bond	D_0 (kcal mol^{-1})	ω (cm^{-1})	D_e (kcal mol^{-1})	R_s (Å)	$F \times 10^{-5}$ (dyn cm^{-1})	Noble gas cluster			
						Bond	D_x (cal mol^{-1})	R_x (Å)	p
H—CH$_2$CH$_2$Cl	97.0	2938	101.2	1.091	5.2	He—Ne	45.4	29.7	1.149
H—CHClCH$_3$	95.7	2991	100	1.091	5.2	He—Ne	45.4	29.7	1.147
Cl—H	102.2	2899	106.4	1.274	5.16$_3$	He—Ar	58.36	3.47	0.958
C—Cl	77.3	681	78.3	1.76	3.44				

Kinetic isotope effect calculations were based on a linear three-atom activated complex model using the value of n^* determined. The calculated values of k_H/k_D are listed in Table 7. The data bear little resemblance to those obtained experimentally, being much lower and showing an inverse temperature dependence. The observed decreasing trend in the values of k_H/k_D with temperature is restored when simple quantum tunnelling corrections are applied. One approximate method uses Bell's correction for an inverted parabolic barrier. The results incorporating this correction are included in Table 7. For hydrogen atom transfers at room temperature the reaction coordinate is non-separable and the application of Bell's tunnelling correction is known to overestimate k_H/k_D. However, the experimental data in Table 7 are still larger by about a factor of 2 than the theoretical results. The use of an unsymmetrical Eckart potential gives even lower values and for this reason they are not reported. The final results are sensitive to changes in

TABLE 7

Comparison of experimental and theoretical values for the kinetic isotope effect in $CH_2DCH_2Cl-CH_2DCH_2Cl$

T (K)	Experimental k_H/k_D	Calculated k_H/k_D[a]	Calculated k_H/k_D[b]
280	5.51	1.10 (1.11)	2.28 (2.75)
290	5.29	1.12 (1.12)	2.25 (2.72)
300	5.08	1.13 (1.14)	2.28 (2.69)
320	4.73	1.16 (1.17)	2.16 (2.62)
340	4.44	1.19 (1.19)	2.09 (2.54)
365	4.14	1.21 (1.22)	2.02 (2.45)

[a] Based on the BEBO method. The first values are based on Pauling's constant 0.28 while those in parentheses employ a value of 0.30.
[b] A tunnelling correction based on Bell's truncated parabola is applied.

some parameters involved in the BEBO calculations. However, when reasonable values are used the resulting changes are small. For instance, an increase in Pauling's constant from 0.28 [10] to 0.30, recommended by Burton et al. [11], results in some improvement (Table 7) but still the gap between the theory and experiment remains. In this light the ostensibly reasonable agreement for CH_3CHDCl must be regarded as fortuitous.

The primary isotope effect is about three times larger for abstraction from the β carbon than from the α carbon for the pair CH_2DCH_2Cl and CH_3CHDCl, in agreement with our earlier investigation of the C_2H_5Cl and C_2D_5Cl system [4]. In both cases, the effects are weaker than the theoretical maxima [12], which indicates an unsymmetrical configuration of the transition state. Here again, the BEBO prediction which suggests a nearly symmetrical structure ($n^* \approx 0.50$) is also in error. According to Lewis [12] the higher the activation energy for hydrogen transfer is, the more symmetrical the transition state and hence the higher the isotope effect. This rule holds well in the present case. Not surprisingly, of the two transition states, $CH_2ClCH_2\cdots H\cdots Cl$ and $CH_3CHCl\cdots H\cdots Cl$, the latter state is expected to be more asymmetric.

Acknowledgment

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