SECONDARY KINETIC ISOTOPE EFFECTS IN HYDROGEN AND DEUTERIUM ABSTRACTION BY CHLORINE ATOMS FROM THE CHLOROMETHYL GROUP IN GASEOUS ETHYL CHLORIDES: EFFECTS OF ISOTOPIC SUBSTITUTION IN THE ADJACENT METHYL GROUP
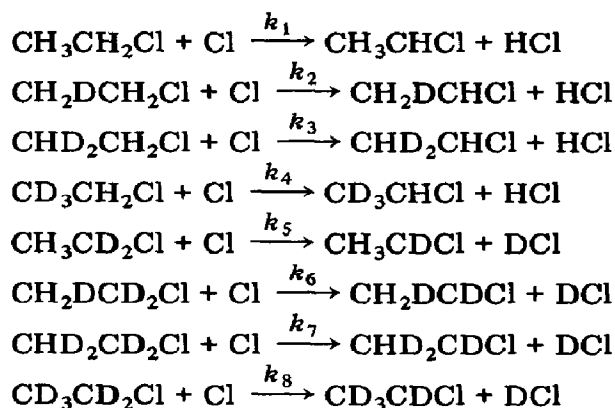
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Summary

Ground state chlorine atoms have been generated photochemically to study the attack on hydrogen in the CH_2Cl group, or deuterium in the CD_2Cl group, as a function of deuterium substitution in the vicinal methyl group of a number of ethyl chloride molecules. The experiments were carried out in the gas phase, at temperatures 9 - 95 °C, using methane as competitor (k_r). Rate constants for the following reactions are reported:

$$CH_3CH_2Cl + Cl \xrightarrow{k_1} CH_3CHCl + HCl$$

$$CH_2DCH_2Cl + Cl \xrightarrow{k_2} CH_2DCHCl + HCl$$

$$CHD_2CH_2Cl + Cl \xrightarrow{k_3} CHD_2CHCl + HCl$$

$$CD_3CH_2Cl + Cl \xrightarrow{k_4} CD_3CHCl + HCl$$

$$CH_3CD_2Cl + Cl \xrightarrow{k_5} CH_3CDCl + DCl$$

$$CH_2DCD_2Cl + Cl \xrightarrow{k_6} CH_2DCDCl + DCl$$

$$CHD_2CD_2Cl + Cl \xrightarrow{k_7} CHD_2CDCl + DCl$$

$$CD_3CD_2Cl + Cl \xrightarrow{k_8} CD_3CDCl + DCl$$

The temperature dependences of the relative rate constants k_i/k_r were found to obey the Arrhenius rate law:

$$\frac{k_1}{k_r} = (1.422 \pm 0.026) \exp\left(\frac{1113 \pm 3}{T}\right)$$

$$\frac{k_2}{k_r} = (1.312 \pm 0.026) \exp\left(\frac{1124 \pm 4}{T}\right)$$

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$$\frac{k_3}{k_r} = (1.305 \pm 0.025) \exp\left(\frac{1130 \pm 3}{T}\right)$$

$$\frac{k_4}{k_r} = (1.237 \pm 0.033) \exp\left(\frac{1145 \pm 7}{T}\right)$$

$$\frac{k_5}{k_r} = (0.981 \pm 0.017) \exp\left(\frac{985 \pm 2}{T}\right)$$

$$\frac{k_6}{k_r} = (0.939 \pm 0.018) \exp\left(\frac{989 \pm 3}{T}\right)$$

$$\frac{k_7}{k_r} = (0.945 \pm 0.018) \exp\left(\frac{990 \pm 3}{T}\right)$$

$$\frac{k_8}{k_r} = (0.904 \pm 0.018) \exp\left(\frac{1005 \pm 4}{T}\right)$$

Error limits are one standard deviation.

The β secondary kinetic isotope effects are close to unity and exhibit a slight inverse temperature dependence. Both the pre-exponential factors and the activation energies decrease as a result of deuterium substitution in the methyl group. The decrease is more pronounced for hydrogen atom abstraction, e.g. $k_1/k_2 > k_5/k_6$. Using the value for $k_9(CH_3CHDCl + Cl \rightarrow CH_3CHCl + DCl)$ determined elsewhere, the α secondary kinetic isotope effect k_9/k_5 was found to be

$$\frac{k_9}{k_5} = (1.10 \pm 0.05) \exp\left(\frac{0 \pm 7}{T}\right)$$

The α effect is much larger than the β effects and is temperature independent.

1. Introduction

Experimental information on secondary kinetic isotope effects in the gas phase is very meagre [1]. For C—H or C—D bond rupture in hydrocarbons or their halogen derivatives these effects arise from the difference in the residual isotopic composition at the carbon atom undergoing reaction (α secondary kinetic isotope effect) or are associated with the isotopic substitution in the adjacent group (β secondary kinetic isotope effect). Since, in these cases, the bonds to the isotopically substituted atom are not made or broken the effects are expected to be very small, which imposes severe demands on the accuracy of analysis. Persky [2] established the existence and estimated the magnitude of an α secondary kinetic isotope

effect from a consideration of the intermolecular and intramolecular primary isotope effects for hydrogen and deuterium abstraction by chlorine atoms from deuterated methanes. The assessment could not be claimed to be accurate, being indirect, and, moreover, it was based on the combination of results obtained in different laboratories, which overlapped only over a narrow temperature range (40 K). In a recent paper from this laboratory [3] the magnitude of the β secondary kinetic isotope effect was established directly by comparing rate data for deuterium abstraction by chlorine atoms from the CD_3 group in CD_3CH_2Cl, CD_3CHDCl and CD_3CD_2Cl. Over the temperature range 10 - 94 °C the overall effect exhibited, surprisingly, a slight "inverse" temperature dependence. Both the pre-exponential factors and the activation energies were found to decrease as a result of deuterium substitution in the adjacent chloromethyl group and the decrements were outside the error limits. The contributions of the two opposing trends made a net effect barely different from unity.

We considered it to be worthwhile to examine whether such trends would be confirmed in other systems. To this end the effect of isotopic substitution in the adjacent methyl group was examined for hydrogen or deuterium abstraction from the chloromethyl group in two sets of compounds: CH_3CH_2Cl, CH_2DCH_2Cl, CHD_2CH_2Cl and CD_3CH_2Cl; CH_3CD_2Cl, CH_2DCD_2Cl, CHD_2CD_2Cl and CD_3CD_2Cl. Aside from yielding direct estimates of the β secondary isotope effects, the results were also used to deduce the magnitude of the α secondary effect (*i.e.* $k(CH_3CD_2Cl)/k(CH_3CHDCl)$) based on the values for the primary kinetic isotope effect in the system $CH_3CH_2Cl-CH_3CHDCl$, reported recently [4].

2. Experimental details

The apparatus, the light source and the experimental procedure have been described previously [5]. Photolyses were carried out in a static system over the temperature range 9 - 95 °C using filtered visible light centred at 424 nm. Only chlorine absorbs the light at this wavelength. Dissociation of an excited chlorine molecule yields virtually thermal chlorine atoms ($Cl\,^2P_{3/2} = 99.2\%$ and $Cl\,^2P_{1/2} = 0.8\%$ at 298 K based on the term value for $Cl\,^2P_{1/2} = 881$ cm^{-1}). The uniformity of the temperature of the reactor was maintained to within ± 0.2 °C and dark reactions were not observed.

The competitive method was employed to determine the relevant rate constants with methane (CH_4) as a reference. The chlorination products of interest, CH_3Cl and 1,1-dichloroethanes (CH_3CHCl_2, CH_2DCHCl_2, CHD_2CHCl_2, CD_3CHCl_2, CH_3CDCl_2, CH_2DCDCl_2, CHD_2CDCl_2 and CD_3CDCl_2), were determined by isothermal (110 °C) gas chromatography (Hewlett–Packard model 5830H) using a 2 m Durapak N column and flame ionization detection. Quantitative analysis involved corrections for the relative sensitivities of the flame ionization detector response, which were accurately determined (see Section 3).

The only other products observed were 1,2-dichloroethanes originating from either hydrogen or deuterium abstraction from the neighbouring methyl group. Although irrelevant from the point of view of this paper, the determination of these compounds could be claimed interesting on its own merit. However, except for CH_3CH_2Cl and CD_3CD_2Cl, the 1,2-dichloroethanes were always formed as a mixture of two different isotopic isomers which could not be resolved using gas chromatography only.

The amounts of plausible secondary chlorination products (dichloromethane, trichloroethanes) were always kept below the limit of detection at the conversions used.

Research grade chlorine, CH_4 and normal ethyl chloride (Matheson) were further purified by vacuum distillations until free of any detectable impurities. The deuterated ethyl chlorides supplied by Merck, Sharp and Dohme (Canada) Ltd. contained methyl chloride as a small impurity. Since the latter compound is the reference product, it was assiduously removed by repeated vacuum distillations below the limit of detection. Some trace amounts of unidentified impurities remained after this purification procedure but were not troublesome. The isotope purity of the ethyl chlorides stated by the manufacturer (above 99% in all cases) was confirmed by independent mass spectral analysis.

3. Results and discussion

The reagents (one of the ethyl chlorides, CH_4 as competitor and chlorine) were photolysed at $\lambda \approx 424$ nm over the temperature range 9 - 95 °C at total pressures of about 21 Torr. Competing reactants were used in twentyfold excess over chlorine to satisfy the demands for the chains to be sufficiently long and for termination to be predominantly by radical combinations [5].

For long chains, the observed photochlorination products originate from the propagation steps according to the sequence

$$RH(RD) + Cl \xrightarrow{k_i} R + HCl(DCl) \tag{1}$$

$$R + Cl_2 \longrightarrow RCl + Cl \tag{2}$$

where R stands for any one of the eight possible α chloroethyl radicals involved (one normal and seven deuterium labelled). At conversions very low with respect to both RH and the reference compound R'H the rate constant ratio can readily be shown to obey the expression

$$\frac{k_i}{k_r} = \frac{[RCl][R'H]_0}{[R'Cl][RH]_0} \tag{I}$$

where the subscript 0 denotes the initial reactant concentrations. The approximations involved in the derivation of this expression have been discussed elsewhere and shown to be justified [5].

TABLE 1

Relative Arrhenius parameters for hydrogen and deuterium abstraction by chlorine atoms[a]

Competitors R_iH-R_jH	n_r [b]	n_m [c]	n [d]	A_i/A_j [e]	$(A_i/A_j)_{corr}$ [f]	$(E_j - E_i)/R$ (K)
$CH_3CH_2Cl-CH_4$	15	18	107	1.394 ± 0.013	1.422 ± 0.026	1113.5 ± 3.0
$CH_2DCH_2Cl-CH_4$	16	7	96	1.274 ± 0.015	1.312 ± 0.026	1124.1 ± 3.5
$CHD_2CH_2Cl-CH_4$	15	8	110	1.256 ± 0.011	1.305 ± 0.025	1130.0 ± 2.7
$CD_3CH_2Cl-CH_4$	14	10	109	1.179 ± 0.024	1.237 ± 0.033	1144.8 ± 6.6
$CH_3CD_2Cl-CH_4$	14	13	110	0.953 ± 0.006	0.981 ± 0.017	985.1 ± 2.0
$CH_2DCD_2Cl-CH_4$	19	7	107	0.904 ± 0.008	0.939 ± 0.018	988.8 ± 3.0
$CHD_2CD_2Cl-CH_4$	19	8	116	0.901 ± 0.007	0.945 ± 0.018	989.5 ± 2.5
$CD_3CD_2Cl-CH_4$	12	12	104	0.853 ± 0.009	0.904 ± 0.018	1005.3 ± 3.5

[a]Stated uncertainty limits are $\pm 1\sigma$.

[b]Number of temperature determinations.

[c]Number of different initial mixtures.

[d]Total number of experiments per set of competitors.

[e]A factor ratios based on assumed relative flame ionization detector sensitivities: S(dichloroethanes) = 1, S(CH_3Cl) = 0.5 (correction factor, 2.0), where S stands for the relative sensitivity.

[f]A factor ratios calculated using the correction factors from Table 2.

Analogous to our previous studies [3 - 5], over the temperature range of this investigation the rate constant ratios were found to conform strictly to the Arrhenius rate law. The results listed in Table 1 are based on the least-squares treatment, and the stated error limits are one standard deviation. It is evident that since the differences in the relative Arrhenius parameters reported in Table 1 are small the success or failure of this investigation depends strongly on the accuracy of analysis. As emphasized earlier [3] the reproducibility of sample preparation rather than the precision of gas chromatographic analyses was the accuracy determining factor. Therefore, many (from seven to 18) different reagent mixtures were prepared using two or three different batches of each ethyl chloride investigated. The random errors, accountable for the error limits quoted in Table 1 under the headings A_i/A_j and $(E_j - E_i)/R$, incorporate uncertainties in the pressure measurement in the preparation of mixtures, varying levels of trace impurities from one mixture to another, and from one sample to another, deviations from homogeneity in gas sampling (if any) and errors in gas chromatographic peak area determinations.

The differences in the flame ionization detector sensitivity towards the compounds of interest is the major contributing factor to the systematic errors. Unfortunately, of the eight 1,1-dichloroethanes determined, only three authentic samples were available to us. These were used to establish the relative correction factors shown in Table 2 with CH_3CHCl_2 arbitrarily chosen as a reference. A discernible isotope effect was observed: a decrease in sensitivity with increasing deuterium substitution in the molecule. One factor contributing to this effect was a noticeable change in retention times,

TABLE 2

Correction factors for the relative sensitivity of the flame ionization detector towards chlorohydrocarbons of interest

RCl	n_d [a]	Correction factor[b]
CH_3CHCl_2		1[c]
CH_3CDCl_2	103	$1.00_9 \pm 0.00_6$
CH_2DCHCl_2		$1.00_9 \pm 0.00_6$[d]
CH_2DCDCl_2		$1.01_8 \pm 0.00_7$[e]
CHD_2CHCl_2		$1.01_8 \pm 0.00_7$[e]
CD_3CHCl_2	95	$1.02_8 \pm 0.00_8$
CHD_2CDCl_2		$1.02_8 \pm 0.00_8$[f]
CD_3CDCl_2		$1.03_9 \pm 0.00_7$[g]
CH_3Cl	109	1.96 ± 0.03

[a] Number of determinations.

[b] The correction factor is defined as $CF = S(CH_3CHCl_2)/S(RCl)$.

[c] 1,1-dichloroethane was arbitrarily chosen as a reference.

[d] The correction factor for CH_2DCHCl_2 is assumed to be equal to that for CH_3CDCl_2.

[e] Values obtained by interpolation from data in Fig. 1.

[f] The correction factor for CHD_2CDCl_2 is assumed to be equal to that for CD_3CHCl_2.
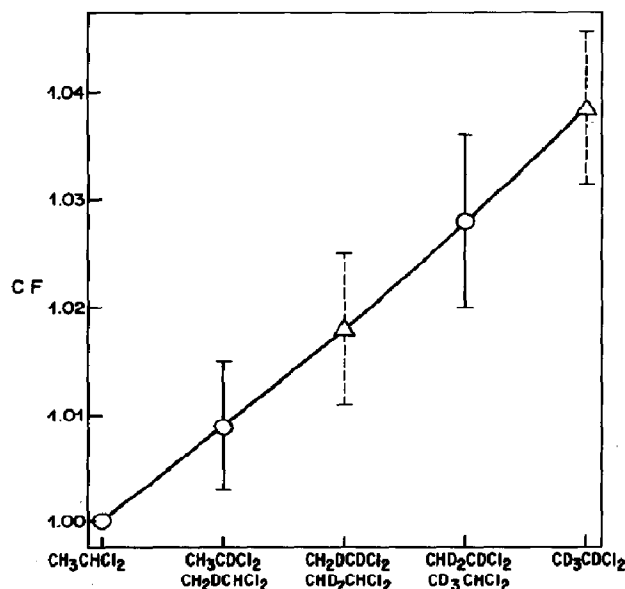
[g] Value obtained by extrapolation from data in Fig. 1.

Fig. 1. Deuterium isotope effect in the flame ionization detector response towards 1,1-dichloroethanes. The correction factor is defined as $CF = S(CH_3CHCl_2)/S(CH_{3-i}D_iCH_{1-j}D_jCl_2)$ ($i = 0$ - 3; $j = 0, 1$): $\bigcirc$, experimental results; $\triangle$, estimates; I, I, error bars.

and hence peak areas, with deuterium substitution. Another factor which may contribute to the overall effect is the ionization process itself. In the case of the other five 1,1-dichloroethanes, samples of which were not

available, the correction factors were estimated by interpolation and extrapolation procedures depicted in **Fig. 1**, on the assumption that isomers having the same number of deuterium atoms would exhibit the same behaviour irrespective of the place of deuterium substitution.

The sensitivity corrections which affect the pre-exponential factor ratios but not the activation energy differences have been taken into account in Table 1 under the entry $(A_i/A_j)_{corr}$.

Other systematic errors, *e.g.* those due to the isotopic impurities, to deviations from the true gaussian distribution and to the assumptions inherent in the simplified reaction mechanism, appear to be insignificant, as discussed previously [3].

3.1. Rate constants and isotope effects

Rate constant ratios for hydrogen and deuterium atom abstraction from the chloromethyl groups at four selected temperatures are listed in Table 3. As expected, the β secondary kinetic isotope effects resulting from deuterium substitution in the adjacent methyl group (β carbon) are, in general, small, close to unity. A slight increment in these effects with increasing temperature can be noted; this increment is largest when all three hydrogen atoms are substituted by deuterium atoms (CH_3CD_2Cl compared with CD_3CD_2Cl and CH_3CH_2Cl compared with CD_3CH_2Cl) but is still within the limits of experimental error. Nevertheless, it seems that the occurrence of this "inverse" effect is established. The same trend has been observed for deuterium abstraction from the CD_3 group in CD_3CH_2Cl, CD_3CHDCl and CD_3CD_2Cl [3]. Furthermore, absolute Arrhenius parameters, listed in Table 4 and based on the absolute rate constant k_{CH_4} ($cm^3 \, s^{-1}$) value for the chlorination of CH_4 reported by Keyser [6]

$$k_{CH_4} = (1.65 \pm 0.32) \times 10^{-11} \exp\left(-\frac{1530 \pm 68}{T}\right)$$ (3)

reveal a distinct trend: both the pre-exponential factors and the activation energies decrease (outside the limits of error) with deuterium substitution

TABLE 3

β 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*
$CH_3CH_2Cl–CH_2DCH_2Cl$	1.044 ± 0.024	1.047 ± 0.023	1.051 ± 0.022	1.053 ± 0.021
$CH_3CH_2Cl–CHD_2CH_2Cl$	1.027 ± 0.021	1.033 ± 0.020	1.038 ± 0.020	1.042 ± 0.019
$CH_3CH_2Cl–CD_3CH_2Cl$	1.028 ± 0.036	1.039 ± 0.035	1.048 ± 0.034	1.056 ± 0.033
$CH_3CD_2Cl–CH_2DCD_2Cl$	1.031 ± 0.020	1.032 ± 0.019	1.034 ± 0.019	1.035 ± 0.018
$CH_3CD_2Cl–CHD_2CD_2Cl$	1.022 ± 0.019	1.024 ± 0.018	1.025 ± 0.017	1.026 ± 0.017
$CH_3CD_2Cl–CD_3CD_2Cl$	1.009 ± 0.022	1.017 ± 0.020	1.023 ± 0.020	1.028 ± 0.019

TABLE 4

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

	A ($\times 10^{-11}$ cm^3 s^{-1})	E_a (cal mol^{-1})
CH_3CH_2Cl[b]	2.33 ± 0.04	828 ± 6
CH_2DCH_2Cl	2.15 ± 0.04	806 ± 7
CHD_2CH_2Cl	2.14 ± 0.04	795 ± 5
CD_3CH_2Cl	2.03 ± 0.05	765 ± 13
CH_3CD_2Cl	1.61 ± 0.03	1083 ± 4
CH_2DCD_2Cl	1.54 ± 0.03	1075 ± 6
CHD_2CD_2Cl	1.55 ± 0.03	1074 ± 5
CD_3CD_2Cl	1.48 ± 0.03	1043 ± 7
CH_3CHDCl	0.89 ± 0.04	1083 ± 15
	1.04 ± 0.04[b]	1218 ± 40[b]
CH_3CHDCl	1.03 ± 0.04	819 ± 20
	1.20 ± 0.04[b]	954 ± 40[b]

[a]The uncertainties in the Arrhenius factors for the reference reaction (CH_4 + Cl → CH_3 + HCl) are not taken into account.
[b]From ref. 4.

in the adjacent group, *i.e.* in going from CH_3CH_2Cl to CD_3CH_2Cl and from CH_3CD_2Cl to CD_3CD_2Cl. This trend is slightly violated for the pair CH_2DCD_2Cl and CHD_2CD_2Cl but the perturbation is minor, and the overall pattern is well preserved. It is worth noting that the hydrogen atom abstraction is more sensitive to the deuterium substitution in the vicinal group than the corresponding abstraction of deuterium atoms. Both hydrogen and deuterium atom abstraction are significantly affected by the substitution of the first and the third hydrogen in the methyl group; the incorporation of the second deuterium atom, *i.e.* the progression from the CH_2D to the CD_2H group, introduces only minute changes, within the limits of experimental error.

The data presented in Table 4, aside from providing the Arrhenius parameters for the β secondary effects, make it also possible to compute the magnitude of the α secondary effect. The data assembled in Table 5 represent the values for the mixed effect: primary and α secondary kinetic isotope effects contribute to the overall values, which, with the use of gas chromatographic techniques, are experimentally non-separable. However, the values for the primary kinetic isotope effect in the system CH_3CHDCl–CH_3CHDCl, obtained by gas chromatography–mass spectrometry (GC–MS) measurements [4], can be used to unravel the α secondary effect indirectly. It is worthy of note that this measured "primary" effect is, in fact, a mixed effect itself, different from the pure primary effect $k(CH_3CH_2Cl)/k(CH_3CHDCl)$ but provides a first-order approximation for what may be considered an iterative process.

TABLE 5

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

	k_i/k_j for the following temperatures			
	280 K	310 K	340 K	370 K
CH_3CH_2Cl–CH_3CD_2Cl[a]	2.293 ± 0.041	2.193 ± 0.038	2.115 ± 0.034	2.057 ± 0.033
CH_2DCH_2Cl–CH_2DCD_2Cl[a]	2.265 ± 0.054	2.161 ± 0.049	2.080 ± 0.046	2.014 ± 0.043
CHD_2CH_2Cl–CHD_2CD_2Cl[a]	2.280 ± 0.048	2.172 ± 0.044	2.087 ± 0.040	2.018 ± 0.039
CD_3CH_2Cl–CD_2CD_2Cl[a]	2.252 ± 0.083	2.146 ± 0.076	2.062 ± 0.070	1.995 ± 0.065
CH_3CHDCl–CH_3CHDCl[b]	1.859 ± 0.071	1.775 ± 0.065	1.709 ± 0.060	1.656 ± 0.057

[a]Present gas chromatography data.
[b]GC–MS data (ref. 4).

The following identity expression holds:

$$\frac{k(CH_3CHDCl)}{k(CH_3CD_2Cl)} \frac{k(CH_3CH_2Cl)}{k(CH_3CHDCl)} = \frac{k(CH_3CH_2Cl)}{k(CH_3CD_2Cl)} \left\{ \frac{k(CH_3CHDCl)}{k(CH_3CHDCl)} \right\}^{-1} \tag{4}$$

The factors on the right-hand side are known from experiment (Table 5). The factors on the left-hand side represent two different α secondary effects which are non-separable. However, on the basis of the reasonable assumption that their magnitudes are similar, a geometric mean value for the α secondary kinetic isotope effect can be obtained from eqn. (4). The results of such calculations, utilizing four independent sets of gas chromatography data against one set of GC–MS data (see Table 5), are shown in Table 6. The values obtained are all close to each other and well within the limits of experimental error. To be sure, the four cases are different in one intrinsic respect: the α secondary kinetic isotope effects (abstraction of a deuterium atom from either the CHDCl or the CDDCl group) are affected by the adjacent methyl groups (CH_3, CH_2D, CHD_2, CD_3). Regrettably, this subtle effect could not be established since the accuracy of the mass spectrometric measurements reported elsewhere [4] was inadequate for this purpose. The average numerical value for the α secondary kinetic isotope effect $KIE_{\alpha\,sec}$ is given by the expression

$$KIE_{\alpha\,sec} = (1.10_5 \pm 0.05) \exp\left(\frac{0 \pm 7}{T}\right) \tag{5}$$

The effect is much larger than the β effects. This could be predicted readily since in the case of the α effects the bond to the isotopic atom undergoes a spatial change, whereas it does not in the case of the β effect. It should be noted that the α effect seems to be independent of the temperature. Thus, the following pattern of temperature dependences emerges: a normal dependence (k_H/k_D decreases with increasing temperature) for the primary effect, no dependence for the α secondary effect and a slight inverse dependence for the β secondary effect. It should be emphasized that this

TABLE 6

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
$CH_3CHDCl-CH_3CD_2Cl$	1.110 ± 0.046	1.111 ± 0.045	1.112 ± 0.043	1.113 ± 0.042
$CH_2DCHDCl-CH_2DCD_2Cl$	1.104 ± 0.050	1.103 ± 0.047	1.103 ± 0.045	1.103 ± 0.044
$CHD_2CHDCl-CHD_2CD_2Cl$	1.107 ± 0.048	1.106 ± 0.046	1.105 ± 0.044	1.104 ± 0.043
$CD_3CHDCl-CD_3CD_2Cl$	1.100 ± 0.058	1.100 ± 0.056	1.099 ± 0.054	1.098 ± 0.052
$MeCHDCl-MeCD_2Cl$[a]	1.105 ± 0.05	1.105 ± 0.05	1.105 ± 0.05	1.105 ± 0.05

[a]Arithmetic average (Me $\equiv CH_3$, CH_2D, CHD_2, CD_3) for α secondary kinetic isotope effects (any β contributions are ignored).

conclusion is valid only over the range of temperatures covered in these studies.

Equation (5) can be used to recalculate the absolute Arrhenius parameters for the reactions $CH_3CHDCl + Cl$ and $CH_3CHDCl + Cl$. The new values, included at the bottom of Table 4, differ somewhat from those reported previously [4]. The former values are also shown for comparison and it is seen that the differences are not serious, but indicate that the error limits for the GC–MS data were underestimated. The new set of values, although obtained indirectly and burdened with the approximations inherent in eqn. (5), is internally consistent and considered to be more reliable.

Acknowledgment

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