be of interest. Evidently, like k_q^T, η also shows a correlation with the electron-releasing nature of para substituents in both of the acetophenone and benzophenone series. One possible explanation for η being less than unity is that the triplet quenching occurs in part via triplet energy transfer (eq 11), the triplet energy (E_T)

$$>\mathrm{C}{=}\mathrm{O}^* + \mathrm{PQ}^{2+} \rightarrow\ >\mathrm{C}{=}\mathrm{O} + \mathrm{PQ}^{2+*} \qquad (11)$$

of PQ^{2+} being 71.5 kcal/mol.[26] While we cannot rule out the involvement of the energy transfer as a parallel process in the triplet quenching in the case of acetophenone (E_T = 74.1 kcal/mol)[27a] and its derivatives, it seems unlikely, from energetic considerations, that energy transfer can be important in the case of benzophenone (E_T = 69.2 kcal/mol)[27a] and its derivatives. For benzophenones, $1 - \eta$ reflects the ease of back electron transfer in the electron-transfer-derived ion pair in the solvent cage producing the reactants in the ground state (in competition with its dissociation into separated radical ions).

Apart from small changes in the location and intensity of absorption maxima, the spectra of the diarylhydroxymethyl radicals are very similar to one another. Among the corresponding triplets, however, significant difference is noticed in the spectra of the 4-methoxy-substituted ones relative to the other 4-substituted benzophenones. The absorption at 440–460 and ~680 nm appears as well-defined maxima in the case of 4-methoxy- and 4,4′-dimethoxybenzophenones, while only shoulders are observed in these spectral regions of T–T spectra of benzophenone and other 4-substituted benzophenones in Table II. An earlier study[28] has recognized the dependence of T–T spectra of substituted acetophenones on the nature of the lowest triplet, $^3(n,\pi^*)$ or $^3(\pi,\pi^*)$. It appears that the methoxy substitution in the para positions of benzophenone brings about a change in the character of the lowest (n,π^*) triplet by mixing a large amount of (π,π^*) character, and this results in intensification of some of the $T_n \leftarrow T_1$ transitions which are otherwise relatively dipole forbidden.

In conclusion, the photoreduction of paraquat via ketyl radicals produced as a result of hydrogen abstraction from alcohols by aromatic carbonyl triplets is complicated by the parallel oxidation of the triplets by paraquat. The kinetic data obtained in the present study should be relevant in designing optimum conditions for photocurrent generation based on these intermediates.

---

(26) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133–139.

(27) (a) Murov, S. L. "Handbook of Photochemistry"; Marcel-Dekker: New York, 1973. (b) Wiberg, K. G. "Physical Organic Chemistry"; Wiley: New York, 1964.

(28) Lutz, H.; Breheret, E.; Lindquist, L. *J. Phys. Chem.* **1973**, *77*, 1758–1762.

Photochlorination of Chloroethane and Chloroethane-d_5

E. Tschuikow-Roux,* T. Yano,[†] and J. Niedzielski[‡]

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

(Received: June 30, 1983)

The hydrogen/deuterium abstraction from C_2H_5Cl and C_2D_5Cl by ground-state chlorine atoms has been investigated between 8 and 94 °C. Results from the internal competition in chloroethane and chloroethane-d_5 combined with the results of external competition with CH_4 as the reference reaction have yielded rate constant data for the following reactions: $CH_3CH_2Cl + Cl \rightarrow CH_3CHCl + HCl$, k_{2s}; $CH_3CH_2Cl + Cl \rightarrow CH_2CH_2Cl + HCl$, k_{2p}; $CD_3CD_2Cl + Cl \rightarrow CD_3CDCl + DCl$, $k_{2s,D}$; $CD_3CDCl + Cl \rightarrow CD_2CD_2Cl + DCl$, $k_{2p,D}$. The temperature dependence of the rate constants (cm^3 s^{-1}) is given by $k_{2s} = (1.43 \pm 0.29) \times 10^{-11} \exp[-(462 \pm 71)/T]$, $k_{2p} = (1.35 \pm 0.28) \times 10^{-11} \exp[-(871 \pm 72)/T]$, $k_{2s,D} = (0.72 \pm 0.14) \times 10^{-11} \exp[-(468 \pm 70)/T]$, and $k_{2p,D} = (0.60 \pm 0.12) \times 10^{-11} \exp[-(1156 \pm 72)/T]$. The results confirm the general trend of chlorine atom attack being faster at the substituted carbon atom. Kinetic isotope effects for the abstraction of primary and secondary hydrogen are k_H/k_D = 5.8 and 2.0 at 298 K, respectively. The magnitude of these relatively weak isotope effects agrees with expectations based on other exothermic chlorination reactions and suggests that in the temperature range of the investigation tunneling does not play an important role.

Introduction

Our recent investigations of the vacuum ultraviolet photolysis of gaseous polychloro and chlorofluoro derivatives of ethane[1-4] have revealed that the principal channel of photodecomposition involves the formation of chlorine atoms produced either directly by rapid, consecutive C–Cl bond cleavage reactions or from the dissociation of an excited Cl_2^* molecule generated by molecular elimination in the primary process. The chlorine atoms so formed undergo competitive reactions involving hydrogen atom abstraction from the parent molecule and addition to the product olefins. Both processes yield halogenated ethyl radicals, albeit with a different energy content. The quantitative interpretation of the results has been somewhat impeded by the lack of, or uncertainty in, the kinetic data of Cl atom reactions with the *halogenated* hydrocarbons. In an effort to gain further insight into the subject we have undertaken a systematic study of the photochlorination of various D-labeled chloroethanes. Aside from the intrinsic interest in the kinetics of these systems, the impetus for this work has been enhanced by the recent renewed attention paid to reactions of atomic chlorine in connection with the chemistry of pollutants.

The objectives of this work were, firstly, to obtain accurate mechanistic and rate data on the H/D abstraction by chlorine atoms. Secondly, to establish the magnitude of the hydrogen/deuterium kinetic isotope effect, which, particularly in the case of atomic chlorine reactions, with low activation energies, is of considerable theoretical interest. Finally, with improved analytical procedures we considered it worthwhile to reexamine some of the older data, but at much lower conversion to minimize complications arising from secondary processes.

[†] Visiting scientist. Present address: Hitotsubashi University, Kunitachi, Tokyo, Japan.

[‡] Visiting scientist. On leave from Department of Chemistry, Warsaw University, Warsaw, Poland.

(1) T. Yano and E. Tschuikow-Roux, *J. Phys. Chem.*, **83**, 2572 (1979).

(2) T. Yano and E. Tschuikow-Roux, *J. Chem. Phys.*, **72**, 3401 (1980).

(3) T. Yano, K.-H. Jung, and E. Tschuikow-Roux, *J. Phys. Chem.*, **84**, 2146 (1980).

(4) T. Yano and E. Tschuikow-Roux, *J. Phys. Chem.*, **84**, 3372 (1980).

0022-3654/84/2088-1408$01.50/0 © 1984 American Chemical Society

Experimental Section

The experiments were carried out in a greaseless, static system of conventional design, using as reaction vessel a 13-cm-long, double-walled, cylindrical Pyrex cell of ca. 160-cm^3 volume (dead volume ~4%). The cell was equipped with two Pyrex windows (40-mm diameter), which were separated by an evacuated space to provide the necessary insulation of the inside of the reactor. Temperature control was achieved by circulating thermostated water through the outside jacket of the cell. The temperature of the bath was maintained to within 0.1 °C. Reaction cell temperatures were determined by copper constantan thermocouples placed at the inlet and outlet positions along the axis of the vessel. Temperature variations along the length of the cell were usually about 0.2–0.3 °C but never exceeded 0.5 °C. The mean value of the readings was then taken as the reaction temperature. The reactants were introduced into the cell by expansion. Preliminary experiments showed that ca. 10-min mixing time was sufficient for the reactant gases to reach ambient temperature and also confirmed that spurious or thermally induced reactions were absent. Pressure measurements were made with a digital fused quartz Bourdon gauge (Texas Instruments, Model 145).

A high-pressure mercury lamp (Osram, HBO 500 W) served as the light source. The optical train consisted of the usual condensing lens, a manually operated shutter, a variable-diameter aperture placed at the focal point of the light beam, a Corning glass filter, followed by a collimating lens, and a fixed aperture equal to the cell diameter. The reaction cell, the feed lines, and the optical assembly were housed in a light-tight enclosure to prevent chain initiation by room or stray light. The absence of such reactions was confirmed by repeated blank analyses. The combination glass filter used (Corning CS 3-73 and CS 5-58) had a maximum transmittance of 18% at 424 nm as determined by a visible/UV monochromator. The transmittance decreased rapidly at shorter wavelengths with an effective zero transmittance at 406 nm. The illumination time was varied between 30 and 40 s depending on experimental conditions.

Product analysis was carried out by flame ionization gas chromatography (Hewlett-Packard, Model 5830 A) using a 2-m-long Durapak N column (*n*-octane on Porasil C) with temperature–time programming between 90 and 105 °C. 1,1- and 1,2-dichloroethane were the only observed products (trichloroethanes, which would be indicative of secondary reactions, were specifically sought, but none were found). The relative sensitivity of the detector response toward both dichloroethanes was determined and routinely checked by using authentic samples. The detector response was found to be less sensitive toward 1,2-dichloroethane under our conditions, and a corresponding correction factor of 1.0482 ± 0.005 was applied. In the competitive photochlorination of CH_4/C_2H_5Cl mixtures, the detector was much less sensitive toward the reference product CH_3Cl, the correction factor being 1.978 ± 0.005 relative to CH_3CHCl_2. The response of the detector toward normal and perdeuterated dichloroethanes was assumed to be equal. Chloroethane-d_5 (98% D) was obtained from Merck Sharp and Dohme and was purified by bulb to bulb vacuum distillations to ensure that the level of impurities was ca. 3 orders of magnitude smaller than the amount of the products. Mass spectral analysis showed that the m/e peaks at 70 ($C_2HD_4{}^{37}Cl$) and 52 ($CHD^{37}Cl$) were negligible, which confirmed the isotopic purity claimed by the manufacturer. The other reactants, C_2H_5Cl, Cl_2, and CH_4, were obtained from the Matheson Co. Ethyl chloride required no additional purification except for the usual degassing under vacuum. The chlorine contained no hydrocarbon or halogenated hydrocarbon impurities. Methane was repeatedly distilled under vacuum, and the residual ethane impurity was ca. 20 ppm.

Results and Discussion

The general scheme for gas-phase photochlorination reactions is well established,[5-7] though careful consideration to experimental conditions must be given to extract useful data. In the case of photochlorination of hydrocarbons the reaction sequence may be represented by the following mechanism:

$$Cl_2 \rightarrow 2Cl \qquad (R1)$$

$$Cl + RH \rightarrow HCl + R \qquad (R2)$$

$$R + Cl_2 \rightarrow RCl + Cl \qquad (R3)$$

$$2R \rightarrow \text{products} \qquad (R4)$$

$$R + Cl \rightarrow RCl \qquad (R5)$$

$$2Cl + M \rightarrow Cl_2 + M \qquad (R6)$$

$$Cl + \text{wall} \rightarrow {}^1/{}_2Cl_2 \qquad (R7)$$

Subject to the usual steady-state approximation and the assumption of long chains, the rate expression for the product yield, under experimental conditions when wall termination (R7) can be safely neglected, is given by

$$d[RCl]/dt = I_a{}^{1/2}k_3[Cl_2]/(k_4 + k_5\gamma + k_6[M]\gamma^2)^{1/2} \qquad (1)$$

where I_a is the absorbed light intensity (photons per unit time per unit volume) and

$$\gamma \equiv [Cl]/[R] = k_3[Cl_2]/k_2[RH] \qquad (2)$$

which also follows from the long-chain assumption. Two limiting cases of interest arise. From eq 2 it is apparent that when $[RH] >> [Cl_2]$, γ can be sufficiently small and radical–radical chain termination is dominant. This leads to the simplified rate law

$$d[RCl]/dt = (I_a/k_4)^{1/2}k_3[Cl_2] \qquad (3)$$

From the stoichiometry of the overall reaction

$$RH + Cl_2 \rightarrow RCl + HCl \qquad (R8)$$

we have $[Cl_2] = [Cl_2]_0 - [RCl]$ and eq 3 can be solved immediately:

$$[RCl]_t/[Cl_2]_0 = 1 - \exp(-kt) \qquad (4)$$

where $k = k_3(I_a/k_4)^{1/2}$, and the subscript zero denotes initial concentration. On the other extreme, if $[RH]_0 << [Cl_2]_0$, γ can be sufficiently large so that only the γ^2 term in eq 1 need to be retained, and eq 1 reduces to

$$d[RCl]/dt = (I_a/k_6[M])^{1/2}k_2[RH] \qquad (5)$$

Between these limiting cases the rate law is dependent on both $[Cl_2]$ and $[RH]$, as given by eq 1 and 2.

For *competitive* photochlorination studies knowledge of the rate law in not necessary provided the chains are long. Nevertheless, it is of interest to establish the range of experimental conditions and to verify the long-chain assumption itself. To this end, in order to test the onset of the validity of eq 4 as a function of the $[RH]_0/[Cl_2]_0$ ratio explicitly, we define the function δ/δ_∞, where

$$\delta \equiv [RCl]_t/[RH]_t = [RCl]_t/([RH]_0 - [RCl]_t) \qquad (6)$$

and

$$\delta_\infty \equiv [RCl]_{t\rightarrow\infty}/[RH]_{t\rightarrow\infty} = [Cl_2]_0/([RH]_0 - [Cl_2]_0) \qquad (7)$$

since, as $t \rightarrow \infty$, $[Cl_2] \rightarrow 0$, $[RCl]_t \rightarrow [Cl_2]_0$, and $[RH]_t \rightarrow [RH]_0 - [Cl_2]_0$. Hence the ratio

$$\frac{\delta}{\delta_\infty} = \frac{[RCl]_t}{[Cl_2]_0}\,\frac{([RH]_0 - [Cl_2]_0)}{([RH]_0 - [RCl]_t)} \qquad (8)$$

---

(5) G. Chiltz, P. Goldfinger, G. Huybrechts, G. Martens, and G. Verbecke, *Chem. Rev.*, **63**, 35 (1963).

(6) F. S. Dainton and P. B. Ayscough in "Photochemistry and Reaction Kinetics", P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Eds., Cambridge University Press, London, 1967, p 64.

(7) G. C. Fettis and J. H. Knox in "Progress in Reaction Kinetics", Vol. 2, G. Porter, Ed., Pergamon Press and Macmillan Co., New York, 1964, p 1.

TABLE I: Dependence of δ/δ_∞ on C_2H_5Cl Pressure for the Photochlorination of C_2H_5Cl[a]

$P(Cl_2)$, torr	$P(C_2H_5Cl)$, torr	C_i/C_j[b]	$10^2\delta$	$10^2\delta_\infty$	δ/δ_∞
0.96	56.0	4.31	0.74	1.74	0.425
0.89	45.2	4.32	0.87	2.01	0.433
0.92	33.8	4.18	1.17	2.80	0.418
0.86	24.0	4.30	1.54	3.72	0.414
0.90	16.8	4.41	2.28	5.66	0.403
0.93	9.4	4.28	3.90	10.98	0.355
0.99	4.5	4.36	6.93	28.21	0.246
1.02	2.2	4.15	8.81	86.44	0.102

[a] Experimental conditions: t(photolysis) = 40 s; $I_a \simeq 10^{17}$ photons s^{-1} cm^{-3}; $T = 298$ K. [b] $C_i/C_j = [CH_3CHCl_2]/[CH_2ClCH_2Cl]$.

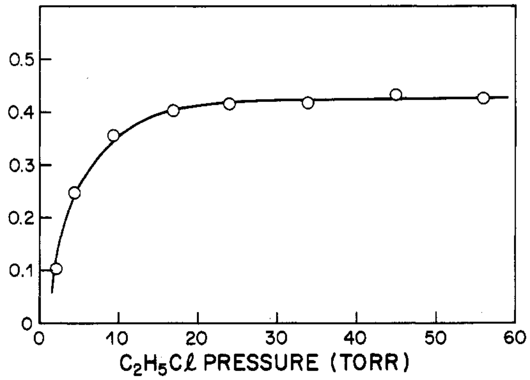

Figure 1. Dependence of the function δ/δ_∞ (eq 8) on chloroethane pressure at $[Cl_2]_0 = 1$ torr, $T = 25$ °C, $t = 40$ s, and constant light intensity.

Equation 8 reduces to eq 4 if the reaction goes to completion. For low conversion, provided $[RH]_0 > [Cl_2]_0$, and hence necessarily $[RH]_0 >> [RCl]_t$,

$$\delta/\delta_\infty \approx ([RCl]_t/[Cl_2]_0)(1 - [Cl_2]_0/[RH]_0)$$

$$\approx [RCl]_t/[Cl_2]_0 \qquad \text{for } [RH]_0 >> [Cl_2]_0$$

and from eq 4

$$\delta/\delta_\infty \approx 1 - \exp(-kt) \tag{9}$$

Therefore, eq 8 with the above conditions predicts that as the ratio of $[RH]_0/[Cl_2]_0$ is increased, δ/δ_∞ should approach a constant value given by eq 9, for a series of runs with the *same* photolysis time, t, and constant light intensity, I_a. Accordingly, corresponding auxiliary photochlorination experiments on C_2H_5Cl were carried out in which the initial concentration of Cl_2 was fixed ($P_{Cl_2} \approx 1$ torr) and the concentration of C_2H_5Cl was varied. Only two reaction products, CH_3CHCl_2 and CH_2ClCH_2Cl (corresponding to internal competition), were observed, and their ratios as well as the total yield were determined. The results are listed in Table I, and a plot of the measured values of δ/δ_∞ as a function of C_2H_5Cl pressure is shown in Figure 1. For fixed values of t, I_a, and $[Cl_2]_0$, the value of δ/δ_∞ increases with increasing C_2H_5Cl pressure, in accordance with eq 8 (where $[RCl]_t$ is the total yield), and reaches a constant value at about $[C_2H_5Cl]_0/[Cl_2]_0 \approx 18$, in accordance with eq 9. Further, with reference to Table I, it should be noted that the product ratio $C_i/C_j = [CH_3CHCl_2]/[CH_2ClCH_2Cl]$ is constant, which is indicative of the validity of the long-chain assumption. Moreover, in another set of preliminary experiments it was confirmed that the product *ratio* does not depend on light intensity, the latter being varied over 4 orders of magnitude.

From the foregoing discussion it is concluded that in the present system the absolute rate law is given adequately by eq 3, and the predominant termination step is reaction R4, provided the substrate/chlorine ratio ≥ 20. Accordingly, in all subsequent chlorination experiments reported in this study we adopted the conditions $P_{Cl_2} \approx 1$ torr and $P_{RH} \approx 20$ torr.

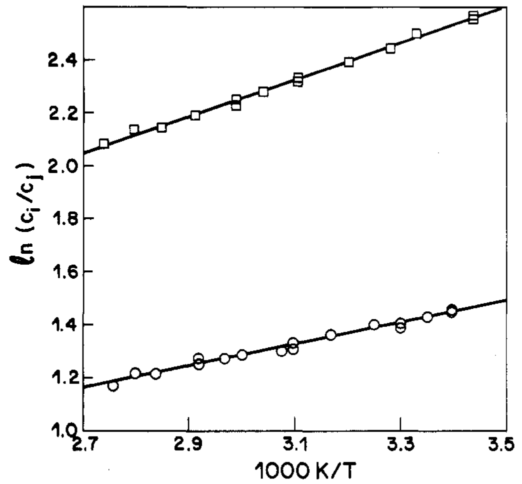

Figure 2. Temperature dependence of the rate ratios for internal competition: $C_i/C_j = [CH_3CHCl_2]/[CH_2ClCH_2Cl]$, circles; $C_i/C_j = [CD_3CDCl_2]/[CD_2ClCD_2Cl]$, squares.

Internal Competition. In this series of experiments pure C_2H_5Cl and pure C_2D_5Cl were photochlorinated as a function of temperature. These systems may be termed internally competitive since the chlorine atom can abstract hydrogen from either the methyl or chloromethyl group. Denoting these hydrogens as primary and secondary, respectively, one can explain the formation of the two observed dichloroethanes in the case of C_2H_5Cl by the following chain-propagation reactions:

$$CH_3CH_2Cl + Cl \rightarrow CH_3CHCl + HCl \qquad k_{2s}$$

$$\rightarrow CH_2CH_2Cl + HCl \qquad k_{2p}$$

$$CH_3CHCl + Cl_2 \rightarrow CH_3CHCl_2 + Cl \qquad k_{3s}$$

$$CH_2CH_2Cl + Cl_2 \rightarrow CH_2ClCH_2Cl + Cl \qquad k_{3p}$$

with analogous reactions for the photochlorination of C_2D_5Cl. Here, it should be noted that the chloroethyl radicals, CH_3CHCl and CH_2CH_2Cl, are thermal and, therefore, can neither decompose nor undergo any internal rearrangement prior to reacting with Cl_2.

For internal competition and long chains, the rate ratio in terms of the product method has the very fimple form

$$\frac{d[R_aCl]/dt}{d[R_bCl]/dt} = \frac{k_{3s}[R_a]}{k_{3p}[R_b]} = \frac{k_{2s}}{k_{2p}} \tag{10}$$

Therefore, the product ratio gives the rate constant ratio for the abstraction reaction directly

$$\frac{k_{2s}}{k_{2p}} = \frac{[CH_3CHCl_2]}{[CH_2ClCH_2Cl]} \tag{11a}$$

and

$$\frac{k_{2s,D}}{k_{2p,D}} = \frac{[CD_3CDCl_2]}{[CD_2ClCD_2Cl]} \tag{11b}$$

These product ratios were found to decrease with increasing temperature for both ethyl chlorides, and corresponding Arrhenius plots are shown in Figure 2. Over the temperature range of this investigation (280–368 K) both plots are linear, and a least-squares analysis yields the expressions

$$\ln(k_{2s}/k_{2p}) = (0.061 \pm 0.04) + (409 \pm 13)/T \tag{12a}$$

and

$$\ln(k_{2s,D}/k_{2p,D}) = (0.191 \pm 0.048) + (688 \pm 15)/T \tag{12b}$$

where the stated uncertainties represent one standard deviation and depict the experimental precision only. Possible systematic errors due, primarily, to uncertainties in temperature and GC calibrations are believed to be small, and reasonable estimates indicate an overall accuracy of ±4% in the activation energy

TABLE II: Relative Rate Parameters[a] for the Internal Competition Cl + C_2H_5Cl and Cl + C_2D_5Cl

compd	A_{2s}/A_{2p}	$(A_{2s}/n_s)/(A_{2p}/n_p)$[b]	$-(E_{2s}-E_{2p})$, cal mol^{-1}	$(k_{2s}/n_s)/(k_{2p}/n_p)$[b] (298 K)	ref
CH_3CH_2Cl	3.16 ± 0.74	4.74 ± 1.11	0 ± 150	4.7 ± 1.7	8
				5.9 ± 0.6	10
	$1.06_3 \pm 0.04_3$	$1.59_5 \pm 0.06_5$	813 ± 26	6.29 ± 0.38	this work
CD_3CD_2Cl	$1.21_0 \pm 0.06_0$	$1.81_5 \pm 0.09_0$	1367 ± 30	18.3 ± 1.3	this work

[a] Stated uncertainties represent ±1σ. [b] Per available H or D atom.

TABLE III: Arrhenius Parameters for the Reaction[a] Cl + $CH_4 \rightarrow CH_3$ + HCl

method[b]	Cl atom source	temp range, K	$10^{12}A$,[c] cm^3/s	E/R,[c] K	$10^{13}k_{298}$, cm^3/s	ref
FP-RF	CCl_4	298			1.51 ± 0.1	14
DF-MS	Cl_2	300-686	50.8 ± 4.5	1792 ± 37	1.24	15
DF-MS	Cl_2	295-490	19.2 ± 5.8	1439 ± 95	1.54	16
CC	Cl_2	220-633	18.8 ± 1.7[d]	1564 ± 31[d]	0.99	17
			21.6 ± 2.4[e]	1571 ± 41[e]	1.11[e]	17[e]
DF-MS	Cl_2	268-423	10.6 ± 4.0	1415 ± 80	0.92	17
FP-RF	CCl_4	218-401	7.44 ± 0.75	1226 ± 55	1.22	18
FP-RF	CCl_4	218-322	7.93 ± 1.53	1273 ± 51	1.10	19
FP-RF	$COCl_2$	299-500	18.4 ± 2.8	1545 ± 52	1.03	20
		200-299	6.51 ± 0.79	1229 ± 27	1.05	
DF-RF	Cl_2	200-300	8.2 ± 0.6	1320 ± 20	0.98	21
		200-500	*f*	*f*	0.99	21
DF-RF	Cl_2	298-423	16.5 ± 3.2	1530 ± 68	0.97	22
		220-298	7.4 ± 2.0	1291 ± 68	1.03	
FP-RF	Cl_2	221-375	*g*	*g*	0.95[h]	23
DF-RF	Cl_2	298			1.08 ± 0.07	24
VLPP	Cl_2	298			0.93 ± 0.05	25

[a] For reevaluated earlier results[9,12,13] based on revised value of $k(\mathrm{Cl} + \mathrm{H_2}) = (4.7 \pm 1.3) \times 10^{-11} \exp[-(2340 \pm 200)/T]$ cm^3/s; see ref 26. [b] FP-RF, flash photolysis-resonance fluorescence; DF-MS, discharge flow-mass spectrometry; CC, competitive photochlorination; DR-RF, discharge flow-resonance fluorescence; VLPP, very low pressure pyrolysis. [c] Uncertainty represents 1 standard deviation. [d] Based on $k(\mathrm{Cl} + \mathrm{C_2H_6}) = (7.84 \pm 0.3) \times 10^{-11} \exp[-(126 \pm 23)/T]$ cm^3/s. [e] Recalculated using revised value for $k(\mathrm{Cl} + \mathrm{C_2H_6})$ from ref 28. [f] Rate constant reported as $k = 8.6 \times 10^{-18} T^{2.11} \exp(-795/T)$ cm^3/s. [g] Arrhenius parameters not reported. [h] Rate constant for $Ar/Cl_2/CH_4$ mixture.

difference and ±6% in the ratio of preexponential factors for both sets of experiments.

We are aware of two investigations reported in the literature which give the difference in reactivity between the two kinds of C–H bonds in ethyl chloride toward hydrogen abstraction by Cl atoms. Cillien et al.[8] determined the relative Arrhenius parameters over the temperature range 30–180 °C and found, within their experimental error, no difference in activation energies between the CH_3 and CH_2Cl groups. These data were then combined with an earlier determination by Pritchard et al.,[9] in which C_2H_5Cl was competitively chlorinated against C_2H_6 but where no distinction was made between the primary and secondary hydrogens, to arrive at approximate absolute rate factors.[8] Wijnen and co-workers[10] studied the photochlorination of CH_3CH_2Cl with and without external competitors at room temperature, using the photolysis of ICl in daylight as a source of chlorine atoms, and reported the relative rates for internal competition at 25 °C. The results of these studies are compared in Table II. The preexponential factor ratio determined by Cillien et al. is about 3 times larger than that reported here; however, these data agree qualitatively in the sense that the *A* factor for chlorine atom attack at the halogenated group is larger. A better comparison of the three sets of data is provided by the rate constant ratios at 298 K (expressed on a per available H atom basis). These ratios agree, within experimental error, and confirm that hydrogen abstraction from the CH_2Cl group is faster than from the CH_3 group. This difference in rate has been explained[10] in terms of the electron-withdrawing power of the highly electronegative Cl atom: the electrons are drawn toward the Cl atom, thus weakening the C–H bonds in the CH_2Cl group. Direct support for this argument is provided by our measured activation energy difference. As can be seen from Table II, the activation energy for the secondary hydrogens in the CH_2Cl group is ca. 813 cal mol^{-1} less than for the primary hydrogens in the CH_3 group. This also corroborates earlier estimates by Franklin and Huybrechts,[11] who obtained $D(\mathrm{CH_3CHCl{-}H}) = 96.7$ kcal mol^{-1} and $D(\mathrm{CH_2ClCH_2{-}H}) = 98.0$ kcal mol^{-1} based on other interpolations.

Competitive Photochlorination of C_2H_5Cl and C_2D_5Cl Relative to CH_4. The determination of absolute rate factors from competitive photochlorination studies requires, naturally, a careful selection of a known reference reaction. The reaction of atomic chlorine with methane

$$\mathrm{Cl} + \mathrm{CH_4} \xrightarrow{k_{2r}} \mathrm{CH_3} + \mathrm{HCl}$$

has recently been the subject of intensive investigations, largely, in response to environmental concern related to the stratospheric ozone depletion by chlorofluorocarbons. Earlier competitive measurements[9,12,13] (relative to H_2) have been superseded, mainly, by direct measurements[14-25] using a number of techniques (Table

---

(8) C. Cillien, P. Goldfinger, G. Huybrechts, and G. Martens, *Trans. Faraday Soc.*, **63**, 1631 (1967).

(9) H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **77**, 2629 (1955).

(10) C. C. Kelly, W. H. S. Yu, and M. H. J. Wignen, *Can. J. Chem.*, **48**, 603 (1970); see also W. H. S. Yu and M. H. J. Wijnen, *J. Chem. Phys.*, **52**, 4166 (1970).

(11) J. A. Franklin and G. H. Huybrechts, *Int. J. Chem. Kinet.*, **1**, 3 (1969).

(12) H. O. Pritchard, J. Pyke, and A. F. Trotman-Dickenson, *J. Am. Chem. Soc.*, **76**, 1201 (1954).

(13) J. H. Knox and R. C. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).

(14) D. D. Davis, W. Braun, and A. M. Bass, *Int. J. Chem. Kinet.*, **2**, 101 (1970).

(15) M. A. A. Clyne and R. T. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1547 (1973).

(16) G. Poulet, G. LeBras, and J. Combourieu, *J. Chim. Phys.*, **71**, 101 (1974).

(17) C. L. Lin, M. T. Leu, and W. B. DeMore, *J. Phys. Chem.*, **82**, 1772 (1978).

(18) R. Watson, G. Machado, S. Fisher, and D. D. Davis, *J. Chem. Phys.*, **65**, 2126 (1976).

(19) R. G. Manning and M. J. Kurylo, *J. Phys. Chem.*, **81**, 291 (1977).

(20) D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, *J. Chem. Phys.*, **66**, 2690 (1977).

(21) M. S. Zahniser, B. M. Berquist, and F. Kauman, *Int. J. Chem. Kinet.*, **10**, 15 (1978).

(22) L. F. Keyser, *J. Chem. Phys.*, **69**, 214 (1978).

(23) A. R. Ravishankara and P. H. Wine, *J. Chem. Phys.*, **72**, 25 (1980).

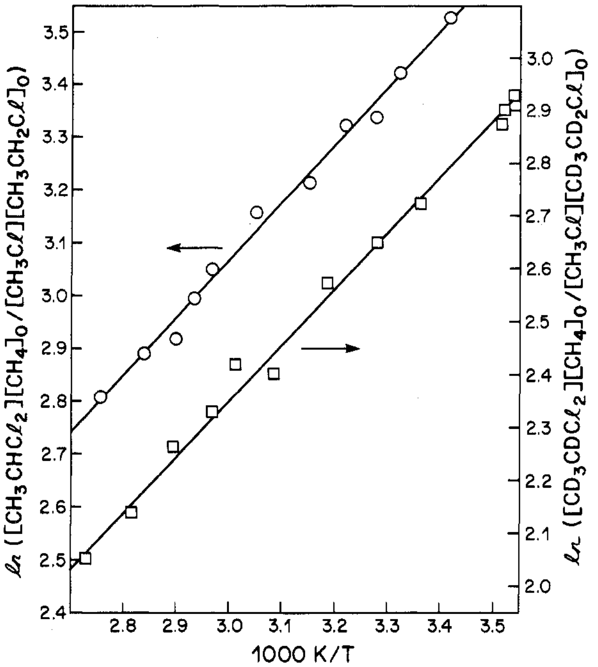

Figure 3. Temperature dependence of the relative rates for H and D abstraction from the α-carbons in CH_3CH_2Cl and CD_3CD_2Cl with methane as a competitor: circles, C_2H_5Cl/CH_4 mixture; squares, C_2D_5Cl/CH_4 mixture.

III). In the temperature range 298–500 K the results are in excellent agreement, and even the discrepancies in the older competitive measurements[9,13] can be resolved if the revised rate data for the primary reference reaction $Cl + H_2 \rightarrow HCl + Cl$ are used.[26] Below room temperature the situation is somewhat less satisfactory.[17] Recent measurements employing the discharge flow–resonance fluorescence (DF–RF)[21,22] and flash photolysis–resonance fluorescence (FP–RF)[20] techniques show that $k(Cl + CH_4)$ exhibits a lesser temperature dependence in the range 200–298 K, which manifests itself in lower apparent Arrhenius parameters. This behavior results in a noticeable curvature (upward) in the Arrhenius plots when these plots encompass the entire temperature range from 200 to 500 K. Although, on theoretical grounds, a strictly Arrhenius behavior is clearly not to be expected, the degree of nonlinearity cannot be predicted, in the absence of detailed information concerning the structure of the transition state. It has been suggested[22] that the non-Arrhenius behavior may be due to some unrecognized secondary reactions that gain in importance in this lower temperature range. Despite these seemingly unresolved questions, at temperatures in the vicinity and above 298 K, the $Cl + CH_4$ reaction provides a most convenient and accurate reference reaction for the present system. We have adopted the rate constant value (in units of $cm^3\ s^{-1}$)

$$k_{2r} = (1.65 \pm 0.32) \times 10^{-11} \exp[-(1530 \pm 68)/T] \quad (13)$$

determined by Keyser[22] for the temperature range 298–423 K using the DF–RF method. This value is in excellent agreement with the rate factors reported recently by DeMore and co-workers[17] obtained from competitive photochlorination and the FP–RF and DF–RF measurements of Whytock et al.[20] and Zahniser et al.,[21] respectively.

For competitive photochlorination of RH with a reference compound R′H, the rate constant ratio is given by[7]

$$\frac{k_2}{k_{2r}} = \frac{\ln\,[RH]_0 - \ln\,[RH]_t}{\ln\,[R'H]_0 - \ln\,[R'H]_t} \quad (14)$$

TABLE IV: Absolute Rate Factors[a] for the Reactions $Cl + C_2H_5Cl$ and $Cl + C_2D_5Cl$ over the Temperature Range 281–367 K

compd		$10^{11}A$, $cm^3\ s^{-1}$	E/R, K	$10^{12}k$, $cm^3\ s^{-1}$ (at 298 K)
CH_3CH_2Cl	k_{2s}	1.43 ± 0.29	462 ± 71	3.03
	k_{2p}	1.35 ± 0.28	871 ± 72	0.726
CD_3CD_2Cl	$k_{2s,D}$	0.72 ± 0.14	468 ± 70	1.50
	$k_{2p,D}$	0.60 ± 0.12	1156 ± 72	0.124

[a] Based on $k(Cl + CH_4) = (1.65 \pm 0.32) \times 10^{-11} \exp[-(1530 \pm 68)/T]\ cm^3\ s^{-1}$; ref 22. Stated uncertainty limits reflect both the precision of the competitive experiments and the uncertainty ($\pm 1\sigma$) in the absolute measurement of the standard reference reaction.

TABLE V: Relative Rate Constants[a] for H/D Abstraction by Cl Atoms (Per Available H/D Atom) at 298 K

	$100[(k_i/n_i)/(k_{C_2H_6}/6)]$				
RH	ref 10[b]	ref 7[c]	ref 19[d]	ref 8[e]	this work[f]
CH_4	2.0	0.26[g]	0.28		
C_2H_6	100	100	100	100	100
$(CH_3)_2CH_2$ (italic CH_3)	110	119[h]			
$(CH_3)_2CH_2$ (italic CH_2)	480	427[h]			
CH_3Cl		1.74[i]	1.71		
$\mathit{CH_3}CH_2Cl$	7.4			12	2.52
$CH_3\mathit{CH_2}Cl$	44			56	15.8
$\mathit{CD_3}CD_2Cl$					0.43
$CD_3\mathit{CD_2}Cl$					7.80

[a] Rate constant for $Cl + C_2H_6 \rightarrow C_2H_5 + HCl$ has been set equal to 100. Unless otherwise indicated, for internal consistency the value of $k(Cl + C_2H_6)$ adopted is that reported in the reference cited. [b] Based on relative products at 25 °C. [c] This review should be consulted for references to original data. [d] Based on direct measurements using the FP–RF technique. [e] Based on approximations; see text. [f] Chosen reference: $k(Cl + C_2H_6) = (9.01 \pm 0.48) \times 10^{-11} \exp[-(133 \pm 15)/T]\ cm^3/s$; ref 28. [g] Direct competition; ref 12. [h] Direct competition; ref 13. [i] From competition pairs CH_3Cl/CH_4 and C_2H_6/CH_4; ref 12.

which is subject to the validity of the long-chain assumption and the absence of complicating features such as secondary chlorination and/or radical reactions other than with Cl_2.

Equation 14 may be expressed in terms of the product yields[27]

$$k_2/k_{2r} = [RCl][R'H]_m/[R'Cl][RH]_m \quad (15)$$

where the subscripts 0, m, and t denote the initial, mean, and final concentrations, respectively. Equation 15 corresponds to a second-order approximation and is accurate up to moderate (~20%) conversions. Under our experimental conditions of $[RH]_0 >> [Cl_2]$, $[R'H]_0 >> [Cl_2]$, and very low conversion, no noticeable error is introduced by replacing $[RH]_m$ and $[R'H]_m$ by the initial concentrations, which corresponds to a first-order approximation. For simultaneous internal competition against an external standard the contributions to the total yield are separable, and one obtains the individual rate ratios directly, e.g.

$$k_{2s}/k_{2r} = ([CH_3CHCl_2]/[CH_3Cl])([CH_4]_0/[CH_3CH_2Cl]_0) \quad (16)$$

The results of the temperature dependence for H and D abstraction from the α-carbons in CH_3CH_2Cl and CD_3CD_2Cl with methane as a competitor are shown in Figure 3, and a least-squares analysis gives the Arrhenius expressions

$$\ln\,(k_{2s}/k_{2r}) = -(0.140 \pm 0.050) + (1068 \pm 21)/T \quad (17a)$$

$$\ln\,(k_{2s,D}/k_{2r}) = -(0.830 \pm 0.050) + (1062 \pm 16)/T \quad (17b)$$

---

(24) J. V. Michael and J. H. Lee, *Chem. Phys. Lett.*, **51**, 303 (1977).

(25) M. H. Baghal-Vayjooee, A. J. Colussi, and S. W. Benson, *Int. J. Chem. Kinet.*, **11**, 147 (1979).

(26) R. T. Watson, *J. Phys. Chem. Ref. Data*, **6**, 871 (1977).

(27) The current state of the art in gas chromatography allows very accurate product analysis, and hence this method is to be preferred over the "consumption" method,[7] particularly at the desirable low conversions. Equation 15 is obtained from eq 14 from a consideration of the carbon mass balance and retention of the first two terms in a power series expansion.

These equations were combined with eq 12a and eq 12b for the internal competition studies to obtain the rate parameters for the abstraction of the primary H and D atoms from C_2H_5Cl and C_2D_5Cl, respectively. Absolute Arrhenius parameters based on the adopted value of k_{2r} are listed in Table IV.

Comparison with Cl + C_2H_6. It is instructive to compare the relative rates of hydrogen atom abstraction from different donors by ground-state chlorine atoms. Table V lists the rates at 25 °C for some selected reactants relative to the Cl + C_2H_6 reaction, for which the rate constant has been set arbitrarily equal to 100. The choice of C_2H_6 as a reference reaction for the purpose of this comparison is predicated by the fact that two of the cited earlier investigations[7,10] used ethane as a competitor. In Table V our rate constant data for the chloroethanes are expressed relative to the value of $k(Cl + C_2H_6)$ determined recently by Lewis et al.[28] using the low-pressure DF–RF technique. Although there is still some disparity in the reported Arrhenius parameters for this reaction,[7,19,28] the remaining differences are small, and the recent absolute values of the rate constant at 25 °C are in good agreement.[28]

An inspection of the data in Table V confirms that the attack of a chlorine atom is faster at the substituted carbon atom in the molecule. Hydrogen abstraction from CH_4 is about 350 times slower than in C_2H_6, which reflects, primarily, the higher C–H bond dissociation energy in CH_4. The relative value for CH_4 determined by Wijnen and co-workers[10] is anomalous in the light of recent determinations (Table III). On the other hand, their respective relative rates for the abstraction of primary and secondary H atoms in propane are in excellent agreement with the data of Knox and Nelson.[13] Turning to the chloroethanes, the difference in reactivity between CH_3CH_2Cl and C_2H_6 is striking, and our data corroborate earlier observations.[8,10] The surprising feature is the low rate of abstraction from the CH_3 group in CH_3CH_2Cl. Wijnen et al.[10] have pointed out that, a priori, one might expect that the rates per available H atom should be roughly equal for the methyl groups in C_2H_6 and in CH_3CH_2Cl but found the rate ratio to be about 14 in favor of H atom abstraction from C_2H_6. Our results for CH_3CH_2Cl suggest that this rate ratio is even higher, being about 40. These observations cannot be solely explained in terms of steric effects caused by the bound Cl atom.[10] Table V shows that the weighted relative rates for the abstraction of primary H atoms from *n*-propane and C_2H_6 are roughly equal. Thus, substitution of one hydrogen by a methyl group has no pronounced effect. Conversely, even though the CH_3 group is larger than the Cl atom, the rate of secondary H atom abstraction from propane is about 11 times,[10] or, as our results would indicate, 27 times faster than the rate of hydrogen abstraction from the CH_2Cl group in CH_3CH_2Cl. A plausible explanation advanced by Wijnen and co-workers[10] for the low rates of Cl atom attack on CH_3CH_2Cl is that the incoming chlorine atom is repelled by the Cl atom in the molecule. It would appear that such a repulsion should be more pronounced at the chlorinated site of the molecule. Nevertheless, the attack on the secondary hydrogen in CH_3CH_2Cl is about 6 times faster. Evidently, there is a concerted effect of repulsion and electron withdrawal by the bound Cl atom in the molecule, in which the latter is predominant. This view is also supported from the comparison[19] of the abstraction of H by Cl in the cases of CH_4 and CH_3Cl, the latter being about 6 times faster, indicating a substantially lower C–H bond dissociation energy in CH_3Cl in accordance with the literature:[29] $D_0{}^0(CH_3\text{–}H) = 103$ kcal mol^{-1} and $D_0{}^0(CH_2Cl\text{–}H) = 98$ kcal mol^{-1}. (*Note Added in Proof.* In a recent communication Weissman and Benson[39] reported $D°_{298}(H\text{–}CH_3) = 105.1$ and $D(H\text{–}CH_2Cl) = 102.9$ kcal mol^{-1}, respectively. While the difference in bond dissociation energies is narrowed, the general trend is preserved.) Nonetheless, it is of interest to note here the FP–RF studies of Michael et al.,[30-32] who reported the rate constants for H abstraction by Cl atoms from CH_3OH (methyl group),[30] CH_3OCH_3,[30] CH_3OOCH_3,[31] and H_2CO[32] over a wide range of temperatures (200–500 K for methanol, dimethyl ether, and formaldehyde; 220–330 K for dimethyl peroxide) and found the rate coefficients virtually invariant with temperature. From a consideration of the corresponding C–H bond dissociation energies (95, 94, ~94, 86 kcal mol^{-1}, respectively) and the C–H bond strength in C_2H_6 (98 kcal mol^{-1}) for which the measured activation energy for H abstraction by Cl atoms is small[28] (~130 cal mol^{-1}), Michael et al. proposed[30] that for *any* R–H molecule with a bond strength of less than ~98 kcal mol^{-1} the H abstraction rates by Cl should be temperature independent and should proceed within a factor of 2 of 1×10^{-10} cm^3 s^{-1}, i.e. approaching the collision rate constant.[31] This empirical correlation seems to be valid for the C_3 and C_4 alkanes[28] but does evidently not apply in the case of ethyl chloride, and any further elaboration would be purely speculative.

TABLE VI: Kinetic Isotope Effects for H/D Abstraction by Cl Atoms at 298 K

RH/R'D	k_H/k_D	$\Delta H°_{298}$, kcal mol^{-1}	ref
H_2/D_2	9.4[a]	1.12	33
	9.36		*b*
CH_4/CD_4	11.8[a]	1.74	33
	13.07		*b*
	9.8		38
CH_2D_2	9.9		34
C_2H_6/C_2D_6	2.8[a]	−5.1	33
	5.88		*b*
	3.4		38
$H\text{–}CH_2CH_2Cl/D\text{–}CD_2CD_2Cl$	5.8_6	−5.2[c]	this work
$H\text{–}CHClCH_3/D\text{–}CDClCD_3$	2.0_2	−6.5[c]	this work
$H\text{–}CCl_3/D\text{–}CCl_3$	4.0[a]	−7.8	33
	2.5		38
$H\text{–}C(Me)_3/D\text{–}C(Me)_3$	1.3	−10.8	38

[a] From a plot of the data in ref 33 according to the Arrhenius rate law. [b] Calculated from reevaluated absolute Arrhenius parameters in "Handbook of Bimolecular and Termolecular Gas Reactions", A. J. Kerr and S. J. Moss, Eds., CRC Press, Cleveland, OH, 1981. [c] Based on heats of formation for CH_2CH_2Cl and CH_3CHCl radicals from ref 11.

Isotope Effects. The measured intermolecular hydrogen/deuterium kinetic isotope effect for H/D abstraction in CH_3CH_2Cl and CD_3CD_2Cl consists of contributions from the primary and secondary isotope effects. Secondary contributions arise since the isotopic composition of the residual chloroethyl groups is different. In this system it is not possible to distinguish between these two contributions; however, in analogy to the methane system, secondary contributions are expected to be small. From an examination of the data for the intermolecular competition in the chlorination of CH_4 and CD_4[33] and the intramolecular competition in CH_2D_2,[34] Persky[35] deduced the temperature dependence of the primary and secondary isotope effects, which shows that at 25 °C the primary effect is about 10 times larger.

Our results are compared with some literature values in Table VI. The magnitude of the observed isotope effect falls within a well-established trend which shows that the kinetic isotope effect decreases with increasing reaction exothermicity and increasing asymmetry of the transition state.[36] A detailed theoretical examination of the kinetic isotope effect is outside the scope of this study and would require knowledge of the structure of the transition state, including a normal-coordinate analysis, and a model calculation of the tunneling correction. An ultrasimple relationship for the hydrogen/deuterium kinetic isotope effect which can serve

---

(28) R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, *J. Phys. Chem.*, **84**, 2009 (1980).

(29) B. deB. Darwent, *Nat. Stand. Ref. Data Ser. (U.S., Nat. Bur. Stand.)*, **31** (1970).

(30) J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Chem. Phys.*, **70**, 3652 (1979).

(31) J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *Chem. Phys. Lett.*, **77**, 110 (1981).

(32) J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, *J. Chem. Phys.*, **70**, 1147 (1979).

(33) G. Chiltz, R. Eckling, P. Goldfinger, G. Huybrechts, H. S. Johnston, L. Meyers, and G. Verbeke, *J. Chem. Phys.*, **38**, 1053 (1963).

(34) K. B. Wiberg and E. L. Motel, *Tetrahedron*, **19**, 2009 (1963).

(35) A. Persky, *J. Chem. Phys.*, **60**, 49 (1974).

to provide a guideline and which has been termed a "theoretical maximum" but which ignores any tunneling correction has been reviewed by Lewis.[36]

$$(k_H/k_D)_{max} = \exp[(E_{Z,RH} - E_{Z,RD})/RT] \qquad (18)$$

Equation 18 is based on a one-dimensional three-particle model in which the zero-point energy difference of the transition states (which would tend to decrease k_H/k_D) is neglected compared to the zero-point energy difference of the reactants RH and RD. On the basis of the harmonic oscillator approximation and the condition of a large mass difference between R and H (whence $\omega_H/\omega_D = 2^{1/2}$)

$$(k_H/k_D)_{max} = \exp[hc(\omega_H - \omega_D)/2kT] = \exp(0.2108\omega_H/T) \qquad (19)$$

where the frequency of vibration ω_H is expressed in cm^{-1}. Application of eq 19 to CH_3CH_2Cl and CD_3CD_2Cl predicts $(k_H/k_D)_{max} \approx 8.0$ and 8.3 for the abstraction from the methyl and chloromethyl group, respectively. Comparison with the values in Table VI shows that $(k_H/k_D)_{max} > (k_H/k_D)_{obsd}$ for both cases. It is of interest to note that the predicted theoretical value is slightly larger for the chloromethyl group, whereas the experimental results show a distinctly opposite trend. Further, since the tunnel correction is always larger than unity and is omitted in eq 19, one can conclude that either quantum-mechanical tunneling in the present system is relatively unimportant or at least it does not compensate sufficiently for the neglect of the zero-point energy difference in the transition states of this simplified treatment. Experimental evidence for the absence of a significant tunnel effect is provided by the temperature dependence of the isotope effects which can be obtained by combining eq 12a,b and 17a,b. Since over the temperature range of this investigation these equations are of the Arrhenius form, the isotope effect is also of this form:

$$\ln(k_{2p}/k_{2p,D}) = (0.82 \pm 0.09) + (285 \pm 33)/T \qquad (20)$$

$$\ln(k_{2s}/k_{2s,D}) = (0.69 \pm 0.07) + (6 \pm 26)/T \qquad (21)$$

An explanation for the "weak" isotope effect must be sought in the asymmetry of the transition state. The dependence of the isotope effect on the symmetry of the transition state was first pointed out by Westheimer.[37] Accordingly, an isotope effect substantially lower than the theoretical maximum (within the simplified three-particle model) is due to the occurrence of a transition state in which the hydrogen is unsymmetrically located between the donor group and the acceptor atom. This effect could as well explain the striking difference in the observed isotope effects for H/D abstraction from the α- and β-carbons in CH_3CH_2Cl and CD_3CD_2Cl. According to Lewis,[36] the following qualitative generalization pertains: "With two hydrogen atom transfers of equal exothermicity, the one of higher activation energy will have the more nearly symmetrical transition state and hence the higher isotope effect". This rule is obeyed in the present case. The higher exothermicity of α abstraction is more than offset by the lower activation energy. Using Lewis' correlation factor, $n = -\Delta H°/E_a$, between the exothermicity and activation energy and the asymmetry of the transition state, $f = 1/(n + 2)$, where f is the fraction of productlike character,[36] we obtain from the data in Tables IV and VI $n = 7.01$ and 3.00 and $f = 0.11$ and 0.20 for the α and β abstraction, respectively. The fact that $f_\alpha < f_\beta$ would explain the weaker isotope effect in the case of H abstraction from the chlorinated carbon atom.

Acknowledgment. The continued financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. C_2H_5Cl, 75-00-3; C_2D_5Cl, 19199-91-8; Cl, 22537-15-1; deuterium, 7782-39-0.

---

[36] E. S. Lewis in "Isotopes in Organic Chemistry", Vol. 2, E. Buncel and C. C. Lee, Eds., Elsevier, Amsterdam, 1976, p 127.

[37] F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

[38] E. S. Lewis, *Top. Curr. Chem.*, **74**, 31 (1978).

[39] M. Weissman and S. W. Benson, *J. Phys. Chem.*, **87**, 243 (1983).

Light Scattering in Aqueous Solutions of κ-Carrageenan

M. Drifford,* P. Tivant, F. Bencheikh-Larbi,† K. Tabti,†

Département de Physico Chimie, C.E.N. Saclay, 91191 Gif-sur-Yvette Cedex, France

C. Rochas, and M. Rinaudo

Centre de Recherches sur les Macromolécules Végétales, Laboratoire Propre du CNRS, Associé à l'Université Scientifique et Médicale de Grenoble, 53X 38041 Grenoble Cedex, France *(Received: May 8, 1983)*

κ-Carrageenan in its Na^+ salt form was investigated by light scattering. Photon correlation spectroscopy was studied as a function of concentration of the polyelectrolyte in 0.1 M NaCl and with zero added salt. The effective diffusion coefficient D_{eff} obtained from the first cumulant enables the hydrodynamic radius of κ-carrageenan at 0.1 M NaCl to be determined ($R_H° \simeq 520$ Å). The angular dissymmetry of the scattered light intensity has been used to obtain the gyration radius in 0.1 M NaCl ($R_G° \simeq 750$ Å). From these data, the "coil" shape of the polysaccharide is confirmed. The electrophoretic light scattering of κ-carrageenan in aqueous solution at low ionic strength gives the electrophoretic mobility, and from the Nernst–Einstein relation, an apparent charge of the polyions has been determined. The evolution of electrophoretic mobility vs. polyion concentration has been analyzed and is in good agreement with Manning's theory. The dynamic behavior of κ-carrageenan in solution at low ionic strength is characterized by interchain interaction with a large correlation length. The experimental data are compared to the theoretical predictions based on the application of the scaling laws to polyelectrolyte solutions.

Introduction

κ-Carrageenan (KC) is an ionic natural polysaccharide extracted from algae. It is a copolymer $(A-B)_n$ that presents the specificity of forming gels in the presence of potassium ions. These gels are thermoreversible and mainly used in food technology. The mechanism of gel formation is still under discussion;[1] nevertheless, the first step may well be a double helix stabilization when K^+ is the counterion.[2] The Na^+ salt of KC may form aggregates,

---

† Stagiaires DGRST

[1] C. Rochas, Thesis, Grenoble, France, 1982.

0022-3654/84/2088-1414$01.50/0 © 1984 American Chemical Society