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Kinetics of the Photobromination of Dichloro- and Dibromoethane. Estimate of the C–H Bond Dissociation Energies and the Heats of Formation of the CH_3CCl_2 and CH_3CBr_2 Radicals

Kikuo Miyokawa* and Eugene Tschuikow-Roux†

Laboratory of Environmental Sciences, Hitotsubashi University, 2-1 Naka, Kunitachi, Tokyo 186-8601

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

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The kinetics of the α-H abstraction reaction $RH+Br\longrightarrow R+HBr$, RH = 1,1-dichloro (**1**) and 1,1-dibromoethane (**2**) was investigated in the temperature range 308—368 K using chloroethane and ethane as an external competitor, respectively. The relative rates were combined with the known rate parameters for chloroethane and ethane to obtain the absolute rate constants ($cm^3\ mol^{-1}\ s^{-1}$): $k_1 = [6.9\pm3.8(\sigma)]\times10^{11}\exp[(-7300\pm360\ \text{cal mol}^{-1})/RT]$ and $k_2 = [2.2\pm1.2(\sigma)]\times10^{11}\exp[(-7110\pm360\ \text{cal mol}^{-1})/RT]$. Using a justifiable approximation concerning the magnitude of the activation energies for the reverse reaction, the following thermochemical quantities (kcal mol^{-1}) were derived: $\Delta H_f^\circ(CH_3CCl_2) = 11.9\pm1.2$, $D^\circ(CH_3CCl_2\text{-H}) = 95.1\pm1.2$, $\Delta H_f^\circ(CH_3CBr_2) = 33.5\pm1.3$, $D^\circ(CH_3CBr_2\text{-H}) = 94.9\pm1.2$. The relation between the reaction thermochemistry and the reactivity in chlorination and bromination of haloethanes is discussed.

Hydrogen abstractions from hydrocarbons by atomic chlorine and bromine are of current interest in connection with atmospheric chemistry in the stratosphere where such reactions terminate ozone depletion by way of Cl–ClO and Br–BrO cycles.[1] Furthermore, reactions with atomic bromine have provided a major method for estimating the enthalpies of formation of the resulting radicals and bond-dissociation energies,[2,3] which are indispensable for understanding the chemical behavior of organic compounds. We previously reported on the kinetics of H-abstraction reactions from C_2H_5X, X = F,[4] Cl,[5] and Br[6] by atomic bromine using the competitive technique, and discussed the effect of halogen substituents on $D^\circ(CH_3CHX\text{-H})$ and $D^\circ(CH_2XCH_2\text{-H})$. In this paper we extend our work to CH_3CHX_2, X = Cl and Br, and report on the kinetics, heats of formation of the CH_3CX_2 radicals and the corresponding C–H bond-dissociation energies for these compounds in order to examine the influence of dihalo subsituents on these quantities.

Experimental

Chemicals. All chemicals used in this study were obtained commercially: C_2H_6 and C_2H_5Cl from Matheson; CH_3CHCl_2 and CH_3CHBr_2 from Eastman Kodak; C_2H_5Br and $CH_3CHBrCl$ from Columbia Organic Chemicals; ACS reagent grade Br_2 from Fisher Scientific Co. Prior to their use, all samples were subjected to the usual trap-to-trap distillation and degassing under vacuum at liquid-nitrogen temperature until no detectable impurities were found by GC analysis.

Measurements. The apparatus, light source, and experimental procedure were the same as reported previously.[5,6] The reaction temperatures ranged from 308 to 368 K and were maintained to within 0.1 K. All GC analyses were carried out on a Varian Vista 6000 gas-chromatograph equipped with a flame ionization detector (FID) and a CDS 401 data processor. Separation was achieved isothermally at 450 K on Porapak N (0.85 m) for $C_2H_4Cl_2/C_2H_5Cl/Br_2$ and at 430 K on Durapak N (0.85 m) for $C_2H_4Br_2/C_2H_6/Br_2$. Photobromination experiments were performed to conversions of roughly 4% or less for each competitor at about 3.6 kPa of the total pressure of the reactants, with the haloethanes being present in ca. 10-fold excess over bromine. Three to four runs were repeated at each temperature.

Determination of the Relative Sensitivities of FID to the Products. The sensitivities (S) of the FID to the products of competitors were determined against ethane. The sensitivity ratios $S(CH_3CHBrCl)/S(C_2H_6)$ and $S(C_2H_5Br)/S(C_2H_6)$ were determined using authentic samples. Since CH_3CBrCl_2 and CH_3CBr_3 were not commercially available, an internal standard method was employed to determine the sensitivity ratios for these compounds. A mixture of CCl_4, RH ($RH=CH_3CHCl_2$ and CH_3CHBr_2) and Br_2 was irradiated at 363 K until about one half of the amount of RH was converted to RBr. From the material balance of RH and the fact that CCl_4 does not react with atomic bromine, Eq. 1 holds:

$$C_i(RH)/C_i(CCl_4) = C_f(RH)/C_f(CCl_4) + C_f(RBr)/C_f(CCl_4), \quad (1)$$

where C_i and C_f represent the initial and final concentrations of the compounds, respectively. Equation 1 can be rewritten in terms of the observed peak area (A) and sensitivity (S) for the respective compounds:

$$\{A_i(RH)/A_i(CCl_4) - A_f(RH)/A_f(CCl_4)\}\cdot S(RH)/S(CCl_4) = A_f(RBr)/A_f(CCl_4)\cdot S(RBr)/S(CCl_4). \quad (2)$$

Since all terms except for $S(RBr)/S(CCl_4)$ can be determined experimentally, the latter can be calculated from Eq. 2, and subsequently converted to $S(RBr)/S(C_2H_6)$. The reliability of this internal standard method was tested by comparing the thus-determined $S(CH_3CHBrCl)/S(C_2H_6)$, $1.04 \pm 0.02(\sigma)$, with that determined using an authentic sample, $1.02 \pm 0.10(\sigma)$. These values agree within the experimental error limits. Therefore, although somewhat complicated and associated with relatively large uncertainties, this internal method is considered to give reliable sensitivities for the two compounds. The sensitivity ratios $S(CH_3CHBrCl)/S(CH_3CBrCl_2) = 1.21 \pm 0.45(\sigma)$ and $S(C_2H_5Br)/S(CH_3CBr_3) = 1.19 \pm 0.06(\sigma)$ were applied to GC data treatments.

Results and Discussion

Kinetics of the Bromination of CH_3CHCl_2 and CH_3CHBr_2. The kinetics of the gas-phase photobromination of CH_3CHCl_2 and CH_3CHBr_2 were studied by the competitive method with external reference compounds. The external competitors chosen were, respectively, CH_3CH_2Cl for CH_3CHCl_2, and C_2H_6 for CH_3CHBr_2 based on the ease of GC separation of the reactants and the products.

The irradiated $CH_3CHCl_2/CH_3CH_2Cl/Br_2$ mixture showed four peaks in the gas chromatogram. The first three peaks were assigned to the two reactants and $CH_3CHBrCl$ by comparing their retention times with those of authentic samples. The fourth peak was deduced to correspond to the anticipated CH_3CBrCl_2 product on the basis that the bromination of CH_3CH_2X (X = F, Cl, Br) and CH_3CHF_2 occurs almost exclusively at the substituted site.[4—7]

Bromination of the CH_3CHBr_2/C_2H_6 mixture also showed four peaks in the chromatogram. Similarly, the first three peaks were assigned to the two reactants and C_2H_5Br, while the fourth peak, with a retention time different from that of an authentic $CH_2BrCHBr_2$ sample, was assigned to the product CH_3CBr_3. In the latter mixture CH_2CHBr was not detected at any temperature examined, this being in contrast to the bromination of CH_3CH_2Br where the formation of a significant amount of CH_2CH_2 was observed at higher temperatures (> 363 K).[6] The formation of CH_2CH_2 was explained in terms of β-hydrogen abstraction from CH_3CH_2Br, followed by Br elimination due to an instability of the incipient radical.[4] Under the present experimental conditions, the bromination of pure C_2H_6 yielded no secondary bromination products.

The competitive technique is so well established[3,8] that it need not be described in detail. The reactions of interest here are the following rate-determining propagation steps:

$$CH_3CHCl_2 + Br \longrightarrow CH_3CCl_2 + HBr, \quad (3)$$

$$CH_3CH_2Cl + Br \longrightarrow CH_3CHCl + HBr, \quad (4)$$

$$CH_3CHBr_2 + Br \longrightarrow CH_3CBr_2 + HBr, \quad (5)$$

$$C_2H_6 + Br \longrightarrow C_2H_5 + HBr. \quad (6)$$

For sufficiently long chains and low conversion (< 5%) with respect to competitors, the reverse reactions may be neglected and the rate constant ratio, without any noticeable error, is simply related to the measured product ratio:

$$k_3/k_4 = [CH_3CBrCl_2][CH_3CH_2Cl]_0/[CH_3CHBrCl][CH_3CHCl_2]_0 \quad (7)$$

and

$$k_5/k_6 = [CH_3CBr_3][C_2H_6]_0/[C_2H_5Br][CH_3CHBr_2]_0, \quad (8)$$

where the subscript 0 denotes the initial concentration of the compound. The validity of Eqs. 7 and 8 was verified over a range of bromine pressure, photolysis time, and initial competitors ratio. Thus, the rate constant ratio, k_3/k_4, was found to be independent of the initial $(CH_3CH_2Cl+CH_3CHCl_2)/Br_2$ mixture pressure ratio 8.61—22.3 (50.0 °C), the irradiation time 8.0—15.0 min (35.8 °C), and initial CH_3CH_2Cl/CH_3CHCl_2 mixture ratio 5.46 and 2.30 (35.8 °C) and 2.30 and 1.50 (71.9 °C); k_5/k_6 was independent of the initial $(C_2H_6+CH_3CHBr_2)/Br_2$ mixture ratio 4.22—28.2 (60.2 °C), the irradiation time 4.5—6.0 min (90.4 °C), and the initial C_2H_6/CH_3CHBr_2 ratio 6.54 and 5.78 (77.0 °C).

Figure 1 shows that the rate constant ratios, k_3/k_4 and k_5/k_6, fit an Arrhenius rate law over the temperature range examined, and a least-squares analysis of the plots yields the following expressions:

$$\ln(k_3/k_4) = -1.953 \pm 0.051 + (1650 \pm 34)/RT \quad (9)$$

and

$$\ln(k_5/k_6) = -6.406 \pm 0.076 + (5550 \pm 50)/RT, \quad (10)$$

where R is in cal K^{-1} mol^{-1} (1 cal = 4.184 J) and the stated uncertainties are one standard deviation. Davies et al.[9] have determined k_6 directly over the temperature range 423—573 K using the laser-flash photolysis of CF_2Br_2 as a source of Br atoms in the presence of C_2H_6, coupled with the time-resolved detection of $Br(^2P_{2/3})$ by resonance fluorescence:

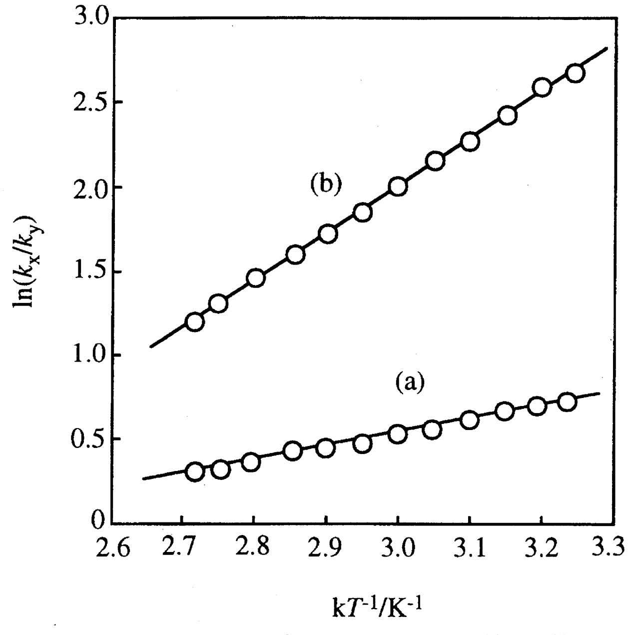

Fig. 1. Arrhenius plots for (a) x = $CH_3C\mathit{H}Cl_2$ and y = $CH_3C\mathit{H}_2Cl$ and (b) x = $CH_3C\mathit{H}Br_2$ and y = C_2H_6.

$$k_6/\mathrm{cm^3\,mol^{-1}\,s^{-1}} = (1.32 \pm 0.72) \times 10^{14} \exp[(-12660 \pm 360)/RT]. \tag{11}$$

We adopt this rate constant as the standard with the tacit assumption that the expression is also valid at temperatures extending below 423 K. From relative measurements of the Br+alkane reaction rates[10] coupled with an absolute measurement for Br+i-C_4H_{10},[11] the k_6 value in the temperature range 298—478 K has been estimated to be

$$k_6/\mathrm{cm^3\,mol^{-1}\,s^{-1}} = (4 \pm 4) \times 10^{14} \exp[(-12700 \pm 600)/RT].$$

Further, the rate-constant ratio k_4/k_6 had been previously determined[5] in the temperature range 313—423 K as

$$\ln(k_4/k_6) = -3.299 \pm 0.045 + (3710 \pm 30)/RT. \tag{12}$$

Combining Eqs. 9, 11, and 12, we obtain

$$k_3 = (6.9 \pm 3.8) \times 10^{11} \exp[-(7300 \pm 360)/RT],$$

and from Eqs. 10 and 11,

$$k_5 = (2.2 \pm 1.2) \times 10^{11} \exp[-(7110 \pm 360)/RT].$$

Table 1 gives the rate parameters for H-abstraction by atomic bromine from CH_3CHX_2 (X = H, F, Cl, and Br).

Thermochemical Quantities for CH_3CHX_2. For any pair of competitive brominations,

$$\mathrm{RH + Br} \underset{r}{\overset{f}{\rightleftarrows}} \mathrm{R + HBr} \qquad \Delta H^\circ(T_\mathrm{m})$$

$$\mathrm{R'H + Br} \underset{r}{\overset{f}{\rightleftarrows}} \mathrm{R' + HBr} \qquad \Delta H^{\circ\prime}(T_\mathrm{m})$$

the difference in the reaction enthalpies is given by

$$\begin{aligned} \Delta H^\circ(T_\mathrm{m}) - \Delta H^{\circ\prime}(T_\mathrm{m}) &= \Delta H_\mathrm{f}^\circ(\mathrm{R}) - \Delta H_\mathrm{f}^\circ(\mathrm{RH}) + \Delta H_\mathrm{f}^\circ(\mathrm{R'H}) - \Delta H_\mathrm{f}^\circ(\mathrm{R'}) \\ &= D^\circ(\mathrm{R\text{-}H}) - D^\circ(\mathrm{R'\text{-}H}) \qquad (13) \\ &= (E_\mathrm{f} - E_\mathrm{f}') - (E_\mathrm{r} - E_\mathrm{r}'), \qquad (14) \end{aligned}$$

where Eq. 14 is written in terms of the activation energies for the forward and reverse reactions and T_m denotes the mean of the temperature range over which the activation energies were measured. An evaluation of the heats of formation and bond-dissociation energies at 298 K requires heat-capacity data. However, the heat-capacity corrections are usually small and are therefore neglected here.

The difference in the activation energies for the forward reactions, $E_\mathrm{f} - E_\mathrm{f}'$, can be measured precisely by the competitive technique, while that for the reverse reactions, $E_\mathrm{r} - E_\mathrm{r}'$, is difficult to measure. Traditionally, the E_r values have been assumed[3] to be of the order of 2±1 kcal mol^{-1}, irrespective of the chemical nature of R, and thus $(E_\mathrm{r} - E_\mathrm{r}')$ was assumed to be 0±2 kcal mol^{-1}. However, recent direct measurements[12] of the temperature dependence of the rate constants for the reverse reaction, R+HBr→RH+Br, where R = CH_3, C_2H_5, $(CH_3)_2CH$, and $(CH_3)_3C$, have shown that the activation energies are small but negative in the range of −0.38 to −1.9 kcal mol^{-1}. The indicated trend is that an increase in the number of electron-donating methyl groups decreases the activation energy. Furthermore, Gutman et al.[13,14] reported that the temperature coefficients for a series of reactions, R+HI→RH+I, where R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, CH_2I, CH_2Br, CH_2Cl, and $CHCl_2$, with activation energies ranging from −1.5 kcal mol^{-1} for $(CH_3)_3C$ to 0.26 kcal mol^{-1} for CH_2Cl, which suggest that the more electronegative substituents require the larger activation energies. These findings imply that the activation energies for the reaction R+HBr→RH+Br with R = haloethyl radical may vary in an analogous manner, reflecting the type and number of halogen substituents, and that the generic approximation $E_\mathrm{r} = 2 \pm 1$ kcal mol^{-1} is less than adequate for the estimation of thermochemical quantities, D°(R-H) and $\Delta H_\mathrm{f}^\circ(\mathrm{R})$.

Recently reported heats of formation of fluoro- and chloroethyl radicals[15—19] derived from ab initio calculation support the above conclusion. The E_r values estimated from Eq. 15 are shown in Table 2 together with the kinetic[4,5,7] and thermochemical data[20—23] used in the calculation.

$$E_\mathrm{r} = E_\mathrm{f} - \Delta H_\mathrm{f}^\circ(\mathrm{HBr}) + \Delta H_\mathrm{f}^\circ(\mathrm{Br}) - \Delta H_\mathrm{f}^\circ(\mathrm{R}) + \Delta H_\mathrm{f}^\circ(\mathrm{RH}). \tag{15}$$

Although the E_r values range from −3.9 to 4.4 kcal mol^{-1}, relatively large E_r values are obtained for only highly fluorinated ethanes ($C_2H_{6-n}F_n$, $n > 3$). The E_r values for the remaining compounds except for CH_3CH_2F fall in a narrow range of 0±1 kcal mol^{-1}.

In order to estimate the thermochemical data for CH_3CHX_2 (X = F, Cl, and Br) we select CH_3CH_2X as the

Table 1. Kinetic and Thermodynamic Data of $CH_3C\mathit{H}X_2$ (X = H, F, Cl, and Br) and CH_3CX_2 Radicals[a]

X	log$A$	E_f	Ref.	$\Delta H_{\mathrm{f},\,298}(CH_3CHX_2)$	Ref.	$\Delta H_{\mathrm{f},\,298}(CH_3CX_2)$	$D^\circ(CH_3CX_2\text{-H})$
H	14.12±0.24	12.66±0.36	9	−20.03±0.10	21	28.36±0.40[b]	100.5±0.4
F	13.35±0.25	13.55±0.36	7[c]	−119.7±1.5	22	−70.4±1.6 −72.3±2[d] −70.7[e]	101.4±1.2 99.5±1[d]
Cl	11.84±0.24	7.30±0.36	f)	−31.1±0.2	21, 23	11.9±1.2 11.8±0.7[g]	95.1±1.2
Br	11.34±0.24	7.11±0.36	f)	−9.3±1.1[h]	24	33.5±1.3	94.9±1.3

a) Units: Pre-exponential(A) factor in cm^3 mol^{-1} s^{-1} and all other quantities in kcal mol^{-1}. b) M. Brouard, P. D. Lightfoot, and M. J. Pilling, *J. Phys. Chem.*, **90**, 445 (1986). c) Original rate parameters are revised taking C_2H_6 as primary reference compound. d) Ref. 25. e) Ref. 15. f) This work. g) Ref. 19. h) The original estimate −9.8 kcal mol^{-1} seems to be a typo and recalculated using the identical scheme.

Table 2. Enthalpies of Formation and Activation Energies for Bromination of Fluoro- and Chloroethanes[a)]

Radical (R)	$\Delta H_{f,\,298}$ (R)[b)]	Ref.	$\Delta H_{f,\,298}$ (RH)	Ref.	E_f(RH+Br)	Ref.	E_r(R+HBr)[c)]
CH_3CHF	−17.3	15	−62.9±0.4	22	10.36±0.37	4	0.2
CH_2FCH_2	−10.7	16	−62.9±0.4	22	12.95±0.39	4	−3.9
CH_3CF_2	−70.7	15	−119.7±1.5	22	13.55±0.36	7	0.0
CH_2FCHF	−56.3	17	−106.0	17	d		
CF_3CH_2	−124.1	16	−178.2±0.4	22	22.46±0.37	7	3.8
CF_3CHF	−164.5	17	−214.1±2	22	18.50±0.39	7	4.4
CHF_2CHF	−108.0	17	−158.9	17	d		
CHF_2CF_2	−157.8±2.1	18	−210.0	18	18.34±0.39	7	1.6
CF_3CF_2	−212.8±1.8	18	−264.0±1.1	22	18.31±0.37	7	2.6±2.1
CH_3CHCl	18.26±0.7	19	26.8±0.3	21	8.95±0.36	5	−0.7±0.8
CH_2CH_2Cl	22.44±0.5	19	26.8±0.3	21	13.14±0.36	5	−0.6±0.7
CH_3CCl_2	11.75±0.7	19	−31.1±0.2	23	7.30±0.36	e	−0.1±0.8

a) Units: kcal mol^{-1}. b) From ab initio calculations. c) Calculated value using Eq. 15. d) Kinetic data has not been reported. e) This work.

reference compounds and, in the absence of *measured* activation energies for the reverse reactions, assign $(E_r - E_r') = 0 \pm 1$ kcal mol^{-1} for a pair of the compounds, taking into account the results of ab initio calculations. With this assumption Eqs. 13 and 14 are reduced to

$$D^\circ(\text{R-H}) = D^\circ(\text{R}'\text{-H}) + (E_f - E_f') - (0 \pm 1)\ \text{kcal mol}^{-1}.$$

The thus-estimated $D^\circ(CH_3CX_2\text{-H})$ and $\Delta H_f^\circ(CH_3CX_2)$ values are given in Table 1 together with the thermochemical data[21—24)] used in the calculation. The $D^\circ(\text{R}'\text{-H})$ and E_f' values for CH_3CH_2X were obtained from an appropriate reference.[4)] Pickard and Rodgers[25)] have estimated $\Delta H_f^\circ(CH_3CF_2) = -72.3 \pm 2$ kcal mol^{-1} from iodination kinetics being slightly lower than the present estimate, while ab initio calculations of $\Delta H_f^\circ(CH_3CF_2)$[15)] $= -70.7$ and $\Delta H_f^\circ(CH_3CCl_2)$[19)] $= 11.8 \pm 0.7$ kcal mol^{-1} from homedesmic reactions agree well with the present estimates.

As Table 1 shows, $D^\circ(CH_3CX_2\text{-H})$ decreases in the order of X: $F \approx H > Cl \approx Br$. The dichloro and bromo substituents weaken the α-C–H bond, while the difluoro substituents apparently exert no influence on the α-C–H bond. This is in contrast to the fact that in the methane analogue the $D^\circ(CHX_2\text{-H})$ decrease in the order of X: X = H (105.1±0.1)[26)] > F (103.2±1)[27)] > Cl (98.4±1.2)[28)] ≈ Br (99.7±1.8 kcal mol^{-1})[28)] and all halogen substituents act to weaken the C–H bond.

The influence of substituents on D°(R-H) has been interpreted qualitatively in terms of the electronic nature of the substituent. The fact that $D^\circ(CHX_2\text{-H})$ are always larger than $D^\circ(CH_3CX_2\text{-H})$ can be explained by the electronic nature of the CH_3 group. Both the σ-inductive effect of the CH_3 group and the hyperconjugative interaction between the CH_3 group and the radical center carbon bring about stabilization of CH_3CX_2 and, hence, weaken the α-C–H bond. A plausible explanation for the different effect of difluoro substituents in CH_2F_2 and CH_3CHF_2 is also sought in the role of the CH_3 group. Recent ab initio calculations of CH_3CX_2 (X = H,[29)] F,[15)] Cl[19)]) showed that the structure of the C–CX_2 moiety is close to planar when X = H and Cl, while being non-planar when X = F. Since the planar structure is in favor of the hyperconjugative interaction, the non-planar structure of the C–CF_2 moiety in CH_3CF_2 causes a decrease in the hyperconjugative contribution of the CH_3 group to the α-C–H bond strength.

Reactivities of Haloethanes toward Cl and Br. The reactivities of haloethanes toward Cl and Br are of interest to understand their behavior in the stratosphere. In general, the influence of halogen substituents on the rate of the RH+Cl (Br)→R+HCl (HBr) reactions has been explained in terms of inductive and mesomeric effects of the substituents, as well as the electronic repulsion between electronegative substituents and the attacking Cl or Br atom.[30)] Figure 2 shows plots of the logarithmic values of the calculated rate constants for

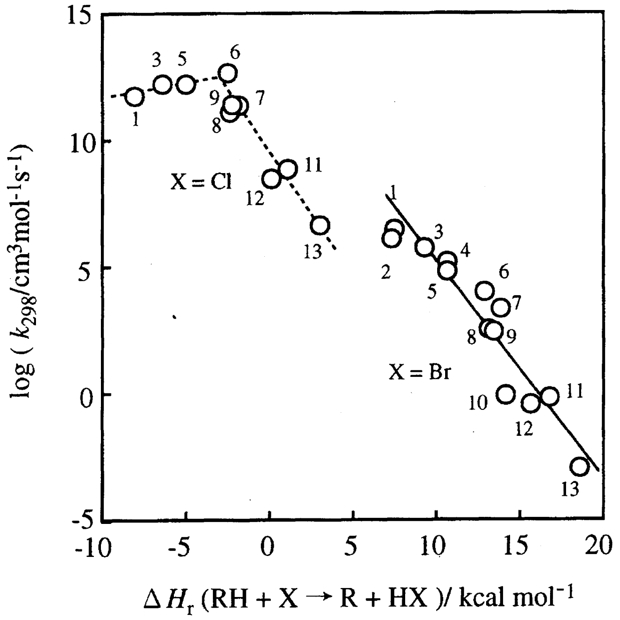

Fig. 2. Relation between ΔH_r and log (k_{298}).
R = CH_3CCl_2 (1); CH_3CBr_2 (2); CH_3CHCl (3); CH_3CHBr (4); CH_3CHF (5); C_2H_5 (6); CH_3CF_2 (7); CH_2CH_2F (8); CH_2CH_2Cl (9); CF_3CHF (10); CF_2CF_2H (11); CF_3CF_2 (12); and CF_3CH_2 (13).

H-abstraction reactions by Cl[30,31] and Br[4,7] atoms at 298 K (k_{298}) per available hydrogen against the reaction enthalpies ($\Delta H^\circ_{\mathrm{r},\,298}$). The heats of reaction for R = CF_3CH_2, CF_3CHF, CF_2HCF_2, CF_3CF_2, CH_2FCHF, CHF_2CHF were calculated from the data given in Table 2 and those for the remaining R are estimates from bromination kinetics.

For bromination an Evans–Polanyi type relation[32] holds between log (k_{298}) and $\Delta H^\circ_{\mathrm{r},298}$, which can be expressed as

$$\log(k_{298}) = -(0.83 \pm 0.08)\Delta H^\circ_{\mathrm{r},\,298} + (13.3 \pm 1.1),$$

and the reaction enthalpy is the predominant factor controlling the reactivities of the haloethanes studied to date. Furthermore, a linear correlation exists between the activation energy (E_f) and D°(R-H) as

$$E_\mathrm{f} = (1.34 \pm 0.11)D^\circ(\text{R-H}) - (121 \pm 11).$$

This can be interpreted by a simple triatomic BEBO calculation[33] for H-abstraction by atomic bromine, which indicates that the transition state has a product-like structure[6] and, hence, the C–H bond strength is a major factor in determining the magnitude of the activation energy. Since the difference in the $H^\circ_{\mathrm{r},\,298}$ values of two compounds is equal to the difference in their D°(R-H) values, the activation energy determines the reaction rate of these compounds.

In the chlorination of haloethanes the reaction enthalpy does not appear to play a major role in determining the observed differences in their reactivity. There is no consistent correlation between the log (k_{298}) and $\Delta H^\circ_{\mathrm{r},\,298}$ values. While log (k_{298}) decreases with increasing endothermicity of reactions involving compounds **7** to **13**, an opposite trend is observed with compounds **1** to **6**. The inflection point lies at around $\Delta H^\circ_{\mathrm{r},\,298} = -2.0$ kcal mol^{-1}. The decreasing reactivity with increasing endothermicity can be merely ascribed to the increasing C–H bond strength in compounds **7** to **13**. For compounds **1**, **3**, and **5** whose activation energies are relatively small, ranging from 0.83 to 1.26 kcal mol^{-1}, the electronic repulsion between electronegative halogen substituents and an attacking Cl atom causes a small increase but being significant in determining the magnitude of their activation energy. The BEBO method which does not incorporate such an intermolecular interaction has been reported not to work for the prediction of activation energy for the chlorination of halogen-substituted methanes and ethanes.[31,34]

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