Kinetics of α - and β -Hydrogen Abstraction from C₂H₅Cl by Br Atoms. Estimate of C–H Bond Dissociation Energies and Heats of Formation of CH₃CHCl and CH₂CH₂Cl Radicals

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The gas-phase photobromination of ethyl chloride has been investigated over an extended temperature range in the presence and absence of ethane as external competitor. The rate constant for α -hydrogen abstraction in CH₃CH₂Cl was redetermined relative to C₂H₆ between 40 and 150 °C. The abstraction of β -hydrogen was measured in the internal competition in the range 70–150 °C by use of electron capture detection. The relative rates were combined with the known rate parameters for the bromination of C₂H₆ [log (A/cm³ mol⁻¹ s⁻¹) = 14.14 ± 0.06, $E = 13.66 \pm 0.14$ kcal mol⁻¹] to obtain the absolute rate constants (cm³ mol⁻¹ s⁻¹) $k(\alpha) = 10^{12.71\pm0.06} \exp[-(9.95 \pm 0.14)/RT]$ and $k(\beta) = 10^{12.60\pm0.07} \exp[-(14.14 \pm 0.15)/RT]$, where the activation energies are expressed in kcal mol⁻¹. From an assessment of thermochemical and kinetic data the following radical heats of formation and C-H bond dissociation energies (kcal mol⁻¹) in C₂H₅Cl have been obtained: ΔH_f° (CH₃CHCl) = 17.6 ± 1, D^o(CH₃CHCl-H) = 96.5 ± 1 and ΔH_f° (CH₂CH₂Cl) = 21.8 ± 1, D^o(CH₂ClCH₂-H) = 100.7 ± 1. These results compare satisfactorily with recent determinations by the monoenergetic electron impact method.

Introduction

Kinetic studies of metathetical atom-transfer reactions and their reverse have provided a major source of thermochemical information, in particular, bond dissociation energies and free radical heats of formation. Bromination and iodination studies have frequently been employed. However, the heats of formation of many haloalkyl or, more specifically, haloethyl radicals are still not known.¹ In this endeavor we have recently reported^{2,3} on the photobromination of CH₃CH₂Cl and CH₃CH₂Br between 32 and 100 °C. Our results, as well as those for CH₃CH₂F and CH₃C-HF₂,⁴ have shown that H abstraction occurs almost exclusively at the substituted site. From the measured activation energies for the forward reactions and interpolated activation energies for the reverse processes, taken in conjunction with the known heats of formation of other relevant species, we obtained the corresponding α -C-H bond dissociation energies and the heats of formation of the CH₃CHF, CH₃CHCl, and CH₃CHBr radicals. The impediment in producing the β -radical by bromine atom attack is due to the large difference in reactivity between the primary and secondary hydrogens and the onset of complicating secondary bromination at the α -position at higher conversion. Quantitative determination of the β -product at low conversion can only be achieved by use of highly sensitive electron capture detection. In the present study we have extended our previous work by measuring the relative rates for α - and β -hydrogen abstraction from CH_3CH_2CI in the presence and absence of C_2H_6 as an external competitor. Rate parameters and thermochemical quantities evaluated by the above-mentioned method are reported.

Experimental Section

The apparatus, light source, and experimental procedure were described previously.² The reactants and all other chemicals used for identification and calibration purposes were obtained commercially² and subjected to the usual trap-to-trap distillation and degassing under vacuum at cryogenic temperatures. Reaction temperatures ranged from 40 to 150 °C and were maintained to within ± 0.1 °C in the interval 40–100 °C and ± 0.2 °C from 100 to 150 °C by circulating a water–ethylene glycol solution through the outer jacket of the cylindrical Pyrex reactor. All analyses were performed isothermally at 175 °C using a Varian Vista 6000 gas chromatograph equipped with a 0.85-m-long Durapak R column and interphased with the CDS 401 data system. Flame ionization (FID) and electron capture (⁶³Ni) detectors (ECD) were used for product analysis as discussed below. The relative sensitivities of the product ratios to both detectors were determined by use

of authentic samples yielding the calibration factors 0.951 ± 0.010 for CH₃CHBrCl/CH₃CH₂Br (FID) and 1.290 ± 0.041 for CH₂BrCH₂Cl/CH₃CHBrCl (ECD). The photobromination experiments were carried out to conversions not exceeding 4% at about 27-Torr total pressure of reactants, the competitors being in ca. 10-14-fold excess over bromine. Three to four runs were repeated at each temperature.

Results and Discussion

Kinetic Data. The very small rate constant for bromine atom attack on the primary hydrogen in C₂H₅Cl prevented the simultaneous determination of rate parameters for both the α - and β -hydrogen abstraction in the presence of the external competitor, C_2H_6 , while maintaining low conversions. Consequently, the rate of α -hydrogen abstraction from C₂H₅Cl was first redetermined relative to ethane over the extended temperature range 40-150 °C. In this series of experiments quantitative product analysis was based on FID gas chromatography. The only bromination products observed were CH₃CHBrCl and CH₃CH₂Br over the entire range of temperature. The abstraction of β -hydrogen was then measured in pure C_2H_5Cl in the range 70-150 °C by the much more sensitive ECD method using the α -hydrogen abstraction as a reference reaction. In this internal competition CH₂BrCH₂Cl and CH₃CHBrCl were observed as major products, the latter in large excess. A secondary bromination product, CH₃CBr₂Cl, was also detected. However, in relation to the primary $\tilde{\beta}$ -product the amount of CH₃CBr₂Cl was negligible above 70 °C but became significant below 60 °C. Since the presence of this secondary bromination product complicates data reduction, the study of β -hydrogen abstraction was restricted to the temperature range 70-150 °C.

The general scheme for internal and external competitive bromination has been reviewed.^{2,5,6} The reactions of interest are the rate-determining propagation steps

$$C_2H_6 + Br \rightarrow CH_3\dot{C}H_2 + HBr$$
(1)

$$CH_3CH_2Cl + Br \rightarrow CH_3CHCl + HBr$$
 (2)

$$\rightarrow$$
 CH₂CH₂Cl + HBr (3)

For sufficiently long chains and conversions of <5% with respect to competitors the reverse reactions may be neglected,¹ and the

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TABLE I: Rate Parameters, Radical Enthalpies of Formation, and Bond Dissociation Energies⁴

R-H	log A	E_{f}	ref	Er	$\Delta H_{\rm f}^{\rm o}({\rm RH})$	$\Delta H_{\rm f}^{\rm o}({\rm R})$	$D^{\circ}(\overline{\mathbf{R}}-\mathbf{H})^{b}$
CH ₃ CH ₂ -H	14.14 ± 0.06	13.66 ± 0.14	4	0.5 ± 0.4^{c}	-20.24 ± 0.12^{d}	28.36 ± 0.4^{e}	100.7
CH ₂ ClCH ₂ -H	12.60 ± 0.07	14.14 ± 0.15	ſ	1.0 ± 1^{g}	-26.83 ± 0.18^{h}	21.8 ± 1^{f}	100.7 ^f
			-			22.8 ± 2^{i}	101.7^{i}
						$21.8 \pm 0.5^{\prime}$	
CH₃CHCI−H	12.71 ± 0.06	9.95 ± 0.14	f	1.0 ± 1^{k}		17.6 ± 1^{f}	96.5 ^f
-						19.3 ± 2^{i}	98.2^{i}
						18.7 ± 2^{j}	
	12.18 ± 0.09	9.14 ± 0.15	2				
СН₃СНГ-Н	13.12 ± 0.08	11.59 ± 0.17	4	1.8 ± 1^{k}	-62.9 ± 0.4^{l}	-17.7 ± 1^{m}	97.3 ^m
CH ₃ CHBr-H	13.18 ± 0.10	11.40 ± 0.16	f, n	1.8 ± 1^{k}	$-15.2 \pm 0.5^{\circ}$	29.8 ± 1^{f}	97.2 ^f
-						$27.3 \pm 2^{\prime}$	94.2
	12.65 ± 0.10	10.58 ± 0.16	3				

^a Units: A factors in cm³ mol⁻¹ s⁻¹; all other quantities in kcal mol⁻¹. ^b Estimated uncertainty in $D^{\circ}(R-H)$ is the same as in $\Delta H_{f}^{\circ}(R)$. ^c Calculated from thermochemistry. ^d Reference 20. ^eReference 18. ^f This work. ^g Assigned the same as in CH₃CH₂Cl. ^hReference 21. ^lReference 25. ^jBy linear interpolation after ref 27; see text. ^kBased on evaluation of halomethanes, ref 19; see text. ^lReference 22. ^mReference 2. ⁿFrom ref 3, recalculated on the basis of revised rate parameters for CH_3CH_2Cl . ^oReference 23.



Temperature dependence of (A) $k_3(CH_3CH_2Cl)/$ Figure 1. $k_2(CH_3CH_2CI)$ and (B) $k_2(CH_3CH_2CI)/k_1(C_2H_6)$.

rate constant ratios are, without noticeable error, simply related to the measured product ratios

$$k_2/k_1 = [CH_3CHClBr][C_2H_6]_0/[CH_3CH_2Br][CH_3CH_2Cl]_0$$
(4)

$$k_3/k_2 = [CH_2BrCH_2Cl]/[CH_3CHClBr]$$
(5)

where the subscript 0 denotes initial concentrations. The validity of eq 4 and 5 was verified over a range of competitor and bromine pressures as follows: For the comparative study with C_2H_6 the relative rates, k_2/k_1 , at 90.5 °C were independent of the initial competitor ratios ($[C_2H_6]_0/[C_2H_5Cl]_0 = 2-10$) and initial bromine pressures (1.3-3.9 Torr) at a fixed total hydrocarbon pressure of 27 Torr. Similarly, in the internal competition at 95.3 °C with $[C_2H_5Cl]_0 = 27$ Torr the rate constant ratios k_3/k_2 were found to be independent of the Br_2 pressure (1.6–3.2 Torr). Accordingly, we have employed in all our subsequent experiments conditions under which eq 4 and 5 have been shown to be valid.

As shown in Figure 1 the rate constant ratios fit an Arrhenius law over the temperature range examined, and a least-squares analysis of both plots yields the expressions

$$\ln (k_2/k_1) = -(3.299 \pm 0.045) + (3711 \pm 32)/RT \quad (40-150 \text{ °C}) \quad (6)$$
$$\ln (k_3/k_2) =$$

$$-(0.255 \pm 0.050) - (4190 \pm 30)/RT$$
 (70-150 °C) (7)

where the stated uncertainties represent one standard deviation. Table I lists the absolute values of the preexponential factors and activation energies for reactions 2 and 3 based on the rate parameters for the bromination of ethane $[\log (A_1/\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 14.4 \pm 0.06; E_1 = 13.66 \pm 0.14 \text{ kcal mol}^{-1}]$ reported by Amphlett and Whittle,⁴ which we discussed and adopted previously.²

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However, in view of some most recent results, some further elaboration as to this choice may be in order. Russell et al.^{7,8} reported a direct investigation of the kinetics and temperature dependence of the reaction $R + HBr \rightarrow RH + Br (R = CH_3, C_2H_5, i-C_3H_7, C_3H_7, C_3H_$ $t-C_4H_9$). For R = $t-C_4H_9$ the reverse reaction was also measured by using a temperature-controlled flash photolysis apparatus with time-resolved detection of Br by atomic resonance fluorescence. The Arrhenius rate constant, $k(Br+i-C_4H_{10})$, determined in this manner was combined⁸ with the relative rate expressions of Fettis and Knox⁹ for $k(Br+C_3H_8)/k(Br+i-C_4H_{10})$ and $k(Br+C_2H_6)/k(Br+i-C_4H_{10})$ $k(Br+C_3H_8)$ to obtain the Arrhenius parameters for reaction 1: $A_1 = (4 \pm 4) \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}; E_1 = 12.8 \pm 0.5 \text{ kcal mol}^{-1}.$ This translates into a rate constant at 298 K which is about a factor of 14 larger than the value obtained from the rate parameters of Amphlett and Whittle.⁴ Furthermore, if the above activation energy is combined with the known thermochemistry for reaction 1 (vide infra), it predicts a slightly negative activation energy for the reverse reaction (-1). In fact, the most noteworthy feature in the investigations of Russell et al. is that in all cases examined^{7,8} they observed a negative temperature dependence, i.e., negative activation energies, which is unprecedented for this class of reactions. The reaction $t-C_4H_9$ + HBr which displayed the largest negative E_a value has been reexamined by Müller-Markgraf, Rossi, and Golden,¹⁰ who find no evidence for a complex mechanism involving a bound intermediate (as was suggested by Russell et al.^{7,8}) and who show that the rate constant increases with temperature as is expected for a simple atom-transfer reaction. Thus, until confirmed, the findings of Russell et al.^{7,8} must be considered as controversial. It is for this reason that we have retained the prior rate parameters of Amphlett and Whittle⁴ for the reference reaction (1).

The extended temperature range in the present study has resulted in a slight upward revision of the Arrhenius parameters for reaction 2 reported previously.² Also listed in Table I for comparison are the data for the α -bromination of C₂H₅F and C_2H_5Br . The rate parameters for C_2H_5Br determined in this laboratory³ relative to CH₃CH₂Cl have been recalculated to reflect the small adjustment noted above.

The activation energy for α -hydrogen abstraction from C₂H₅Cl is ca. 3.7 kcal mol⁻¹ lower than in C_2H_6 , which may be rationalized in terms of polar effects and contributing resonance stabilization of the incipient CH₃CHCl radical, such stabilization being absent in C_2H_5 . In contrast, the activation energy for primary hydrogen

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abstraction in C_2H_5Cl is somewhat higher than in C_6H_6 . Although the difference is small ($\sim 0.5 \pm 0.2 \text{ kcal mol}^{-1}$), it may not be insignificant. An explanation of this deactivation of the β -hydrogen must be sought in an inductive effect, whereby the electron deficient methyl group impedes the attack by the electrophilic bromine atom. Such polar effects have been considered to be major factors controlling the rate of hydrogen abstraction in chlorination¹¹⁻¹³ and bromination^{11,13,14} studies. However, there is a marked difference between the former and the latter. Thus, whereas in the exothermic chlorination of CH3CH2Cl both secondary and primary hydrogens are significantly deactivated relative to ethane, 12,15-17 just the opposite is true for hydrogen abstraction from the chloromethyl group in the endothermic bromination reaction, and the difference in selectivity between the α - and β -hydrogens is much larger than in chlorination. The preexponential factors for reactions 2 and 3 are lower than for the bromination of ethane and parallel the general trend observed in the photochlorination of haloethanes.^{16,17} However, the difference in the A factors is so small that the reactivity between α - and β -hydrogen abstraction is governed almost entirely by the large activation energy difference, $E_3 - E_2 = 4.2 \pm 0.2 \text{ kcal mol}^{-1} (k_3/k_2)$ $= 2.7 \times 10^{-3}$ at 100 °C).

Thermochemical Quantities. The evaluation of thermochemical quantities, $\Delta H_{f}^{\circ}(\mathbf{R})$ and $D^{\circ}(\mathbf{R}-\mathbf{H})$, from kinetic data requires knowledge of the activation energies for the forward and reverse reactions. The activation energies for reactions -2 and -3 have not been measured. On the other hand, the reaction enthalpy for the bromination of C_2H_6 can be calculated with considerable confidence. With the newly established $\Delta H_1^{\circ}_{298}(C_2H_5) = 28.36$ \pm 0.4 kcal mol^{-1 18} and the well-known heats of formation for all the other species, $\Delta H^{\circ}_{298}(1) = 13.15 \pm 0.4 \text{ kcal mol}^{-1}$. The activation energy for reaction 1 is $E_f(C_2H_6) = 13.66 \pm 0.14$ kcal $\text{mol}^{-1,4}$ and hence $E_r(C_2H_6) \simeq 0.5 \pm 0.4$ kcal mol⁻¹. This is not in agreement with the small negative activation energy for this reaction $[E_r(C_2H_6) = -0.8 \pm 0.2 \text{ kcal mol}^{-1}]^8$ as mentioned above. However, for reactions of the type $R + HBr \rightarrow RH + Br$, the activation energies are generally small, and the conclusion which can be drawn is that, for $R = C_2H_5$, E_r is near zero. The thermochemistry for the bromination of methane is known equally well, or even better, and $E_r(CH_4) = 1.04 \pm 0.2 \text{ kcal mol}^{-1.2}$ On the basis of the difference between $E_r(C_2H_6)$ and $E_r(CH_4)$, we have proposed² the correlation

$$E_r(C_2H_5X) \simeq E_r(CH_3X) + [E_r(C_2H_6) - E_r(CH_4)]$$
 (8)

For the halomethanes (X = F, Cl, Br) the activation energies for the reverse reactions have been evaluated previously.¹⁹ Thus, with reference to the process

$$\mathbf{R}\mathbf{H} + \mathbf{B}\mathbf{r} \stackrel{1}{\longleftrightarrow} \mathbf{R} + \mathbf{H}\mathbf{B}\mathbf{r} \tag{9}$$

we have the thermochemical relations

$$\Delta H_{f}^{\circ}(\mathbf{R}) = \Delta H_{\mathbf{R}}^{\circ} - \Delta H_{f}^{\circ}(\mathbf{HBr}) + \Delta H_{f}^{\circ}(\mathbf{RH}) + \Delta H_{f}^{\circ}(\mathbf{Br})$$
(10)

$$D^{\circ}(\mathbf{R}-\mathbf{H}) = \Delta H_{\mathbf{R}}^{\circ} + D^{\circ}(\mathbf{H}-\mathbf{Br})$$
(11)

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where the reaction enthalpy is given by $\Delta H_{\rm R}^{\circ} = E_{\rm f} - E_{\rm r}$. The results are listed in Table I based on the known heats of formation of ethane,²⁰ haloethanes,²¹⁻²³ and other species.²⁴ It should be noted that no heat capacity corrections have been applied to the calculated $\Delta H_f^{\circ}(\mathbf{R})$ and $D^{\circ}(\mathbf{R}-\mathbf{H})$ values since the requisite structural and spectroscopic data are not available. However, for the mean temperature of these kinetic studies such corrections are very small¹⁹ and well within the uncertainties of the estimated activation energies for the reverse reactions.

Our results for the thermochemical quantities are within the stated error limits of recent determinations by Holmes and Lossing²⁵ using monoenergetic electron impact on selected precursor molecules to generate the haloethyl radicals as the neutral fragment. The agreement is deemed satisfactory, particularly if one allows for the fact that the data reduction by Holmes and Lossing required heats of formation of the precusor molecules which were derived by group additivity. The latter is less accurate for compounds involving bromine owing to a smaller data base on which the additivity scheme is based. Thus, use of $\Delta H_{\rm f}^{\rm o}$ - $(CH_3\dot{C}HBr) = 27.3 \pm 2$ kcal mol⁻¹ reported by Holmes and Lossing leads to $E_r(CH_3CH_2Br) = 4.35 \pm 2 \text{ kcal mol}^{-1}$, which we believe to be too high.

It is also worthy of note that the bond energy for the primary C-H bond in ethyl chloride, $D(CH_2ClCH_2-H) = 100.7 \pm 1.1$ kcal mol⁻¹, derived from the present bromination study is, within the estimated uncertainty, the same as in ethane. Again, this result contrasts sharply with deductions based on measured activation energies for the corresponding chlorination reactions^{15,17,26} and supports indirectly our earlier observation³ that in the chlorination of the ethane/haloethane series there is no correlation between activation energies and reaction enthalpies. Further, our results lend support to the procedure adopted by Franklin and Huybrechts²⁷ to estimate the heats of formation of chlorine-substituted ethyl radicals based on the assumption that all primary, secondary, and tertiary C-H bonds in the chloroethane series have the same values. In their evaluation Franklin and Huybrechts used as anchor points the then accepted $D(C_2H_5-H)$ value for primary hydrogen and an average of $D(CH_2ClCCl_2-H)$ and $D(C_2Cl_5-H)$ for tertiary hydrogen to obtain the C-H bond energy for secondary hydrogen by linear interpolation. Adopting the same procedure, but using the revised values (in kcal mol⁻¹) of $D(C_2H_5-H) = 100.7$ ± 0.4 ,¹⁸ $D(C_2Cl_5-H) = 95 \pm 2$,¹ and $D(CHCl_2CCl_2-H) = 94 \pm 2$ 2^1 and the newer recommended value $\Delta H_f^{\circ}(C_2H_5Cl) = -26.83$ \pm 0.18 kcal mol⁻¹,²¹ leads to the heats of formation of the ĊH₂CH₂Cl and CH₃ĊHCl radicals which are also listed in Table I. The agreement with our values is well within the stated uncertainties.

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Registry No. CH2ClCH3, 75-00-3; CH3CH2Br, 74-96-4; H2, 1333-74-0; Br•, 10097-32-2; CH2CH2Cl, 16519-99-6; CH3CHCl, 16520-13-1; CH₃CHBr, 16520-14-2.

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