Kinetics and thermochemistry of the $R + HBr \Rightarrow RH + Br$ ($R = CH_2Cl, CHCl_2, CH_3CHCl \text{ or } CH_3CCl_2$) equilibrium

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The kinetics of the reactions of CH₂Cl, CHCl₂, CH₃CHCl and CH₃CCl₂ with HBr have been investigated in a heatable tubular reactor coupled to a photoionization mass spectrometer. The radicals, R, were produced homogeneously in the reactor by pulsed 248 nm exciplex laser photolysis. The decay of R was monitored as a function of HBr concentration under pseudo-first-order conditions to determine the rate constants as a function of temperature and pressure range. The reactions were studied separately over a wide temperature range and at these temperature ranges the rate constants determined were fitted to an Arrhenius expression (error limits stated are 1σ + Student's t values, units in cm³ molecule⁻¹ s⁻¹): $k(CH_2Cl) = (6.6 \pm 1.7) \times 10^{-13} \exp[-(4.1 \pm 0.2) \text{ kJ mol}^{-1}/RT]$, $k(CHCl_2) = (4.1 \pm 1.0) \times 10^{-13} \exp[-(9.8 \pm 1.0) \text{ kJ mol}^{-1}/RT]$, $k(CH_3CHCl) = (3.0 \pm 0.9)$ × $10^{-13} \exp[+(3.0 \pm 0.2) \text{ kJ mol}^{-1}/RT]$ and $k(CH_3CCl_2) = (4.4 \pm 0.9) \times 10^{-13} \exp[-(5.9 \pm 0.7) \text{ kJ mol}^{-1}/RT]$. The kinetic information obtained was combined with the what is known of the recently measured rate constants of the reverse reactions to calculate the entropy and the heat of formation values of the radicals studied. The thermodynamic values were obtained at 298 K using a second law procedure. The results for entropy values are as follows (units in J K⁻¹ mol⁻¹): 271 ± 7 (CH₂Cl), 280 ± 7 (CHCl₂), 279 ± 6 (CH₃CHCl) and 288 ± 5 (CH₃CCl₂). The results for $\Delta_{\rm f}H_{298}^{\circ}$ are as follows (units in kJ mol⁻¹): 117.3 ± 3.1 (CH₂Cl), 89.0 \pm 3.0 (CHCl₂), 76.5 \pm 1.6 (CH₃CHCl) and 42.5 \pm 1.7 (CH₃CCl₂). The C-H bond energy of analogous chlorinated hydrocarbons derived from the enthalpy of reaction values are as follows (units in kJ mol⁻¹): 419.0 \pm 2.3 (CH₃Cl), 402.5 \pm 2.7 (CH_2Cl_2) , 406.6 ± 1.5 (α -C-H bond in CH_3CH_2Cl) and 390.6 ± 1.5 (α -C-H bond in CH_3CHCl_2). Improved heats of formation for the CH₂ClO₂ radical, $\Delta_f H_{298}^{\circ}(CH_2ClO_2) = -(4 \pm 11)$ kJ mol⁻¹, and for the CHCl₂O₂ radical, $\Delta_f H_{298}^{\circ}(CHCl_2O_2) = -(17 + 11)$ \pm 7) kJ mol⁻¹ are also calculated from the previously measured R' + O₂ \rightleftharpoons R'O₂ (R' = CH₂Cl or CHCl₂) equilibriums.

The heats of formation of small alkyl and halogenated alkyl free radicals have been investigated and in some cases reinvestigated during the past ten years.¹⁻⁴ As the experimental setups used for the kinetic measurements have been improved, the free radical reactions needed for thermochemical calculations and for computer modelling purposes have been measured under time-resolved conditions. In particular, the values of the heats of formation of large alkyl free radicals have been redetermined as the accuracy of kinetic experiments have been improved.^{1,2} However, the thermochemical data based on a time-resolved kinetic investigations of polyatomic free radicals containing halogen atom(s) is almost exceptional in the literature. The current study attempts to improve on this imperfection by making an experimental investigation to determine the heats of formation of four partly chlorinated saturated alkyl free radicals, CH_2Cl , $CHCl_2$, CH_3CHCl and CH_3CCl_2 .

Chlorinated free radicals, such as the radicals investigated in the current study, can be considered to have a central role in the oxidation and pyrolysis processes of chlorinated wastes, such as municipal wastes containing chlorine-bearing polymeric materials. The polyatomic halogenated free radicals in these oxidation and pyrolysis processes most likely consist only of chlorinated C_1 and C_2 free radicals because the larger species containing longer carbon chains do not live long enough to undergo chemical reactions to any significant extent with the other reactants. The radicals investigated in the current study can be formed, for instance, by Cl atom abstraction reaction with CH₃Cl, CH₂Cl₂, CH₃CH₂Cl and CH_3CHCl_2 . The other chlorinated C_1 and C_2 alkyl and alkenyl radicals can generally be formed by Cl atoms abstracting H atoms from chlorinated hydrocarbons which on the other hand are associated with the formation of highly toxic chlorinated dibenzodioxins and dibenzofurans in combustion

processes. All four of the radicals investigated most likely have considerable lifetimes at elevated temperatures so as to undergo secondary radical-radical and radical-molecule reactions in a combustion process, where these reactions can produce larger chlorinated hydrocarbons. Such a product formation may start for example by a multichannel reaction for CHCl₂ either with itself or with CH₃ or CH₂Cl. These reactions are very exothermic and they proceed through an energetic addition complex, which dissociates to the products of the reaction. Because of the high exothermicity of the reaction many reaction channels are open for product formation. After their formation, the larger chlorinated hydrocarbons also undergo reactions with free radicals but they may also dissociate unimolecularly to form a stable unsaturated molecule and an atom. The reactions of these species can not be resolved only by computer modelling, accurate experimental laboratory investigations are also needed to understand the complex reaction mechanism.

The chemical kinetics of CH_2Cl , $CHCl_2$, CH_3CHCl and CH_3CCl_2 with HBr have not previously been studied. The kinetics of these free radicals is investigated here in order to obtain thermochemical properties of the radicals. The approach is similar to that used previously for polyatomic alkyl free radical reactions with HI⁵ and HBr.^{6,7}

Experimental and Kinetics

Description of experiments

The rate constants of the reactions of CH_2Cl , $CHCl_2$, CH_3CHCl and CH_3CCl_2 with HBr were measured as a function of temperature and pressure. The experimental apparatus used has been previously described.^{8,9} Briefly, pulsed, unfocused 248 nm radiation from a Lambda Physik EMG 201 MSC exciplex laser operated at 5 Hz was collimated and then directed along the axis of a heatable Pyrex or quartz reactor. The 10.5 mm i.d. reactor was coated with different materials

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to reduce heterogeneous reactions. These included halocarbon wax,† poly(dimethylsiloxane)‡ and boric oxide. Gas flowing through the tube at 5 m s⁻¹ was completely replaced between laser pulses. The flowing gas contained the radical precursor (typically below 0.1%), HBr (in varying concentrations) and the carrier gas, He, in large excess (>98%). An axial pressure drop along the reactor (accounted for in calculating the concentrations of reactants) was typically in the range 1.1-3.4% and an estimate for a typical radial diffusion value was between 2 and 8 mm² ms⁻¹ at the conditions used for the investigations.¹⁰ Gas was sampled through a 0.44 mm i.d. hole located at the end of a nozzle in the wall of the reactor and was formed into a beam by a conical skimmer before it entered the vacuum chamber containing the quadrupole mass filter. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from 10-30 ms before each laser pulse and 16-25 ms after the laser pulse with a multichannel scalar. Data from 1000 to 13 500 repetitions of the experiments were accumulated before the data were analysed by a non-linear least-squares analysis program.

The only photolysis wavelength used to generate radicals was 248 nm. At this wavelength it is practically impossible to photodissociate the reactant, HBr, to a measurable extent.¹¹ In many previous radical + HBr studies the shorter, 193 nm, exciplex laser radiation was used to photogenerate the radicals.^{2,6,7} At this wavelength HBr is photodissociated to reactive H and Br atoms. If these atoms are generated in considerable amounts, they can influence the values of the observed kinetics, making them too high. The other advantage of using 248 nm photolysis instead of 193 nm photolysis is the ability to generate the radical of interest with less excess internal energy. Furthermore, from what is known about vibrational deactivation of a small polyatomic radical,^{12,13} there is a reason to believe that, under the experimental conditions used in the current study, this relaxation occurs rapidly (<0.5ms) compared with the observed reaction time (16-25 ms).

Kinetic results

The chemical kinetics of the following four metathetical reactions were studied in a flow reactor:

$$CH_2Cl + HBr \rightarrow CH_3Cl + Br \tag{1}$$

$$CHCl_2 + HBr \rightarrow CH_2Cl_2 + Br$$
(2)

$$CH_3CHCl + HBr \rightarrow CH_3CH_2Cl + Br$$
 (3)

$$CH_{3}CCl_{2} + HBr \rightarrow CH_{3}CHCl_{2} + Br$$
(4)

The information obtained was combined with the rate constants of the reverse reactions [(-1), (-2), (-3) and (-4)], $^{2.14-16}$ § in order to calculate the heats of formation and the experimental entropy values of the radicals studied. As expected, the reactions investigated did not show any pressure dependence at the pressure range used in the current study. The results obtained from all the experiments to measure reactions (1)-(4) are given in Table 1.

Photogeneration of radicals

Four alkyl halides were used as precursors. They were photodissociated at 248 nm to an extent of 1-2%. The CH₂Cl radical was generated after photolysing CH₂ClBr. At 248 nm, bromochloromethane has two photodissociative channels, where the formation of CH₂Cl and Br radicals seem to be a major channel. This conclusion was drawn after comparing the radical signals qualitatively:

$$CH_2ClBr \rightarrow CH_2Cl + Br$$
 (5a)

$$\rightarrow$$
 CH₂Br + Cl (5b)

The formation of bromomethyl radical is a very minor route compared with the formation of CH_2Cl radical. Tzeng *et al.* have used translational spectroscopy to study the photodissociation of bromochloromethane at 193 and 248 nm.¹⁷ They found the molecule to be dissociated only in reaction (5a) at 248 nm.

The CHCl₂ radical was generated after photolysing CHCl₂Br. Bromodichloromethane has three plausible photolysing routes at 248 nm:

$$CHCl_2Br \rightarrow CHCl + Cl + Br$$
 (6a)

$$\rightarrow CCl_2 + HBr$$
 (6b)

$$\rightarrow$$
 CHCl₂ + Br (6c)

The primary products are CHCl₂ and Br. Photodissociation [path (6b)] produces the very reactive carbenoid, CCl_2 , which regenerates the radical after reacting with HBr during the first ms after laser radiation. This side-reaction appeared as a small flat displacement on the ion signal monitored for the kinetics of $CHCl_2 + HBr$ reaction. However, its contribution to the ion signal was always < 10% and was subtracted from it as a constant value before the decay monitored was fitted by a non-linear least-squares procedure. The influence of the CCl₂ radical was found not to be important by using an alternative radical source to generate the CHCl₂ radical. The radical was generated by the fast reaction between Cl atoms and CH₂Cl₂ at room temperature where the measured and the calculated (from the Arrhenius expression) rate constants of reaction (2) differs most from each other. Cl atoms were formed by photolysing SO_2Cl_2 at 248 nm. It photodissociated to a 1-2% extent to produce practically only SO₂ and Cl atoms. The decays from two different experiments where different radical sources were used for the kinetics of reaction (2) are practically the same (see Table 1).

The CH₃CHCl radical was generated from 1-bromo-1chloroethane. The major photolysing channel is the dissociation of the C-Br bond of the precursor. The possible isomerization of the α -C₂H₄Cl to the β -C₂H₄Cl form by an H atom shift via a three-membered cyclic transition state is negligible at the conditions used in the current study. Of these two isomers the α -C₂H₄Cl radical is more stable than the β -C₂H₄Cl radical, which starts to decompose unimolecularly at 420 K at the pressures used in the current study. These radicals also have different kinetics in their reactions with HBr.¹

The CH₃CCl₂ radical was generated from 1,1,1-trichloroethane. It has only one meaningful photolysis channel at 248 nm to produce an α,α -dichloroethyl radical and a Cl atom. However, the absorption cross-section of the precursor at 248 nm seems to be quite small at low temperatures. This prevented the extension of the investigations of reaction (4) below 457 K.

Data analysis

Experiments were conducted under pseudo-first-order conditions where HBr existed in great excess compared with the concentration of radicals. Only two radical reactions had significant rates under these conditions:

$$R + HBr \rightarrow RH + Br$$
 (1), (2), (3) or (4)

$$\mathbf{R} \rightarrow \text{heterogeneous loss on the wall}$$
 (7)

[†] Halocarbon wax is a product of the Halocarbon Wax Corp. Hackensack, NJ, USA.

[‡] Poly(dimethylsiloxane), 200 fluid was obtained from Aldrich.

 $C_p^{\circ}(CH_2Cl_2)$ at 298 and 433 K was measured as 51.6 and 59.3 J K⁻¹ mol⁻¹, respectively.¹⁶ The preliminary results of the reaction of CH₃CHCl₂ + Br has been obtained for this study from Dr. Tschuikow-Roux.

Tª/K	10^{-16} [He]/atom cm ⁻³	10^{-14} [HBr]/molecule cm ⁻³	k_{7}/s^{-1}	wall coating ^b	$10^{14}k_i^{\rm c}/{\rm cm}^3~{\rm s}^-$
		Reaction: $CH_2Cl + HBr \rightarrow CH_3Cl$	$l + Br(k_1)$		
299	5.82	2.6-7.8	6.5	HW	12.8 ± 0.4
300	17.7	2.1-6.2	6.6	HW	13.2 ± 0.7
348	5.83	1.9-13	7.1	HW	14.8 ± 0.5
348	5.89	5.0-13	8.1	PDMS	16.9 ± 0.5
409	5.84	4.3-11	6.6	PDMS	17.5 ± 0.9
510	5.87	0.8–11	13	PDMS	23.2 ± 1.3
510	5.88	2.8-11	1.7	B_2O_3	24.6 ± 0.7
677	5.89	2.7-11	4.1	B_2O_3	34.5 ± 1.3
	$k_1 = (6.6 \pm$	$1.7) \times 10^{-13} \exp[-(4.1 \pm 0.2) \text{ kJ mol}^-$	$^{1}/RT$]cm ³ molec	$ule^{-1} s^{-1}$	
		Reaction: $CHCl_2 + HBr \rightarrow CH_2Cl$	$_{2} + Br(k_{2})$		
295	5.78	9.7-18	15	PDMS	2.51 ± 0.22^{d}
299	5.82	6.7–18	4.1	HW	3.07 ± 0.12
300	17.8	7.2–29	5.2	HW	3.95 ± 0.26
348	5.87	8.8–19	4.8	HW	3.15 ± 0.33
409	5.85	5.2-14	24	PDMS	3.36 ± 0.34
409	5.84	6.4-21	7.1	PDMS	3.04 ± 0.20
454	5.84	4.0-14	11	PDMS	3.37 + 0.41
510	5.86	5.4-15	7.5	PDMS	4.23 ± 0.31
584	5.87	5.4-15	5.6	B ₂ O ₃	5.12 ± 0.43
677	5.89	2.5-16	1.2	B ₁ O ₁	7.17 + 0.17
799	5.90	4.0-16	0.7	B_2O_3	9.85 ± 0.44
	$k_2 = (4.1 \pm$	1.0) × 10 ⁻¹³ exp[-(9.8 ± 1.0) kJ mol ⁻	$^{1}/RT$]cm ³ molec	$ule^{-1}s^{-1}$	
		Reaction: $CH_3CHCl + HBr \rightarrow CH_3CH$	$H_2Cl + Br(k_3)$		
300	5.80	0.46–2.4	15	HW	98.9 ± 7.8
300	17.8	0.40-2.5	16	HW	82.6 ± 4.4
348	5.83	0.51-2.4	13	HW	90.6 ± 4.3
348	5.91	0.70-3.0	15	PDMS	88.6 ± 2.8
409	5.85	1.02-3.5	14	PDMS	75.1 ± 2.1
510	5.84	0.85-3.7	13	PDMS	60.0 ± 1.5
510	5.87	1.71–16	10	B_2O_3	56.5 ± 1.1
677	5.88	0.87-5.7	6.3	B_2O_3	56.0 ± 2.0
	$k_3 = (3.0 \pm$	0.9) × 10 ⁻¹³ exp[+(3.0 ± 0.2) kJ mol ⁻	$^{1}/RT$]cm ³ molec	$ule^{-1} s^{-1}$	
		Reaction: $CH_{3}CCl_{2} + HBr \rightarrow CH_{3}CH_{3}CH_{3}$	$\operatorname{ICl}_2 + \operatorname{Br}(k_4)$		
457	5.83	4.5-13	13	B ₂ O ₃	9.70 ± 0.80
511	5.86	1.1-11	11	$\overline{B_2O_3}$	11.6 ± 0.60
579	5.87	4.2–17	7.1	B_2O_3	13.0 ± 0.70
579	11.9	3.8–13	4.5	B ₂ O ₃	12.2 ± 0.60
667	5.90	3.5-17	2.0	B ₂ O ₃	15.3 ± 0.23
787	5.95	5.2–16	2.8	$\tilde{B_2O_3}$	18.3 ± 0.60
	$k = (AA \pm$	$(0.0) \times 10^{-13} \text{ exp} [(5.0 \pm 0.7) \text{ k J mol}^{-1}]$	1/RT cm ³ molec	$ule^{-1}e^{-1}$	-

Table 1 Conditions and results of experiments used to measure the rate constant of the reaction $R + HBr \rightleftharpoons RH + Br$ ($R = CH_2Cl$, $CHCl_2$, CH_3CHCl or CH_3CCCl_2)

^a Temperature uncertainty: ± 2 K (295-409 K) and ± 4 K (454-799 K). ^b Wall coating materials used: HW = halocarbon wax, PDMS = [poly(dimethylsiloxane)], and B₂O₃. ^c Errors are 1σ + Student's t and based on statistical uncertainties. ^d The radical was generated from the reaction of Cl + CH₂Cl₂.

In all sets of experiments the initial radical precursor concentration was adjusted to be so low that radical-radical or radical-atom reactions had negligible rates compared with reactions (1), (2), (3), (4) or (7). This was ensured by comparing the measured first-order wall-loss decays, k_7 , of the radical with that produced (in the absence of HBr) at different conditions where precursor concentration was held steady but the laser radiation was attenuated by a factor of 2 using quartz plates (the radical concentration was changed by the same factor). The decays from these different experiments were equal with respect to their statistical error limits.

Bimolecular rate constants for reactions (1), (2), (3) and (4) were obtained from the slopes of plots of the exponential radical decay constant k' vs. [HBr] {from $[\mathbb{R}^+]_t = [\mathbb{R}^+]_0 \exp(-k't)$ }, where $k' = k_{1,2,3 \text{ or } 4}$ [HBr] + k_7 . A representative ion signal decay profile and a decay constant plot from two sets of experiments to measure k_4 and k_1 are shown in Fig. 1 and 2. Only the product of reaction (1) was detectable. It was found to be CH₃Cl and is shown in Fig. 2. The other products from reactions (2)–(4) could not be detected. This is not peculiar in view of the difficulties of detecting stable products from HBr or HI reactions. The appearance potential of the radical from the product of these reactions is often lower in energy

than the ionization potential needed to detect the stable product. Monitoring the product by atomic resonance radiation causes it to be fragmented at the radical mass number thus increasing the background of the adjacent product mass number as well. A high background makes signal/noise ratio poor.

Secondary reactions

There exists in flow-tube experiments the possibility of two different kind of reactions, namely a reaction in the gas phase and a heterogeneous reaction. Furthermore, the latter reaction can appear as an unimolecular or a bimolecular reaction on the wall of the reactor. A heterogeneous unimolecular reaction, k_7 , (often termed a wall reaction, k_w) is taken into account in the data analysis, but there is always a possibility of a heterogeneous bimolecular reaction occurring between the reactants during experiments. This phenomenon in R + HBr reactions is not limited to the reaction of a radical with HBr at the wall, but also a reaction between the radical and Br₂ may happen at the wall also. It can easily be proven that HBr can be adsorped onto almost any kind of surface including Pyrex glass (and especially onto a metal surface) and



Fig. 1 Plot of first-order decay constant k' vs. [HBr] for one set of experiments conducted to measure the $CH_3CCl_2 + HBr$ rate constant, k_4 , at 667 K. Insert in the lower right corner is the ion signal profile of $CH_3CCl_2^+$ recorded during one of the experiments shown as a solid circle ([HBr] = 1.19×10^{15} molecule cm⁻³) in the linear regression fit. The line through the data in the insert is an exponential function fitted by a non-linear least-squares procedure. The first-order decay constant for $CH_3CCl_2^+$ in the displayed ion signal profile is (185.7 ± 2.8) s⁻¹. The insert in the upper left corner partly shows the mass scan taken during one experiment to demonstrate the generated CH_3CCl_2 radical in a laser pulse. The ratio of peak areas of signals at different mass numbers relates directly to the abundance of different isotopes of the CH_3CCl_2 radical.

will be decomposed to produce Br₂ and H₂ as a result of a catalytic reaction. The reactions of radicals with Br₂ are systematically faster (for example, in the case of CH₃ and C₂H₅ radicals, about by a factor of 12 at room temperature) than their reactions with HBr.¹⁸ The presence of bromine on the wall of the reactor can presumably most influence the radical reactions, which are very fast with Br₂ because the amount of bromine produced on the wall by heterogeneous reaction may be limited to a monolayer in a chemisorption process. In this case, according to the Langmuir isotherm,¹⁹ adsorption depends strongly on pressure at low carrier gas densities and will reach a maximum value when the pressure is increased. To minimize the possible influence of heterogeneous wall reactions, different wall coating materials were used (see Table 1 for more details). A great effort was used to set up experimental conditions where the heterogeneous reactions mentioned above were not present. The first-order decay plots used to calculate the bimolecular rate constants of the reaction did always show a linear dependency of k' vs. [HBr]. A non-linear dependency is a sign of a possible adsorption of HBr on the wall of the reactor.

Accuracy of measurements

The error limits stated in Arrhenius expressions are 1σ + Student's t and they are based only on the statistical uncertainties. The reactions were studied under pseudo-first-order conditions when it was needed to know accurately only the concentration of HBr. HBr concentration was measured conventionally, directing HBr flow to a known volume through a needle valve and the increasing pressure in the volume was measured as a function of time, $\Delta p/\Delta t$. The concentration of HBr was then calculated from the ideal gas law equation using the measured pressure change, $\Delta p/\Delta t$, with the



Fig. 2 Plot of first-order decay constant k' vs. [HBr] for one set of experiments conducted to measure the CH₂Cl + HBr rate constant, $k_{1,}$ at 409 K. Insert in the lower right corner is the ion signal profile of CH₂Cl⁺. The first-order decay constant for CH₂Cl⁺ in the displayed ion signal profile is (81.9 ± 2.0) s⁻¹. The insert in the upper left corner is the product, CH₃Cl⁺, of reaction (1) monitored at the same HBr concentration as the radical. The ion signal recorded is fitted also by a non-linear least-squares procedure. The rise-constant of CH₃Cl⁺ product formation equals (84.4 ± 7.1) s⁻¹.

previously determined flow rate of the carrier gas, gas density, and temperature and pressure in the reactor. The flow rate of HBr was measured before and after the kinetic experiments. These HBr concentration determinations differed typically <2% from each other. The mean value of these determinations was used for the second-order rate-constant calculations. The measurement of the first-order decay constants, k', was repeated at different HBr concentrations up to six times to increase the significance of the experiment by increasing the statistical degree of freedom. Measured first-order decay constants at known HBr concentrations were used together for calculating the bimolecular rate constant, k. The other errors including temperature and flow rate were always <1%. The bimolecular rate constants of reactions (1)–(4) were weighted by their error limits and fitted to the two-parameter Arrhenius expression.

Reagent sources and purification procedures

The gases and liquids used were obtained from Aldrich (bromochloromethane, 99%; bromodichloromethane, >98%; dichloromethane, 99.6%; SO_2Cl_2 , 97%; 1,1,1-trichloroethane, 99.5%; and hydrogen bromide, 99%), Lancaster (1-bromo-1-chloroethane, 98%) and Matheson (helium, 99.995%).

The carrier gas, He, was used as provided. The free-radical precursors were degassed by using freeze-pump-thaw cycles. HBr was collected in a flow trap kept at 77 K and was repeatedly distilled to remove any traces of bromine. Pure HBr existed as a white solid at the temperature of liquid nitrogen and was stored in a dark Pyrex bulb. The gas handling system, which was used to set up a known HBr flow to the reactor gas inlet, was made from Pyrex glass and Teflon tubes.

Photoionization energies used

Reactants and products of the photolysis as well as the precursors were photoionized using atomic resonance radiation. A neon lamp (16.7, 16.9 eV) was used to detect SO_2Cl_2 , SO_2 , Cl, Cl₂ and SO_2Cl . An argon lamp (11.6, 11.8 eV) was used to detect CH₂ClBr, CHCl₂Br, CHCl, CH₃CHBrCl, CH₃CCl₃, HBr, Br₂ and Br and a chlorine lamp (8.9–9.1 eV) to detect CH₂Cl, CH₂Br, CHCl₂, CH₃CHCl and CH₃CCl₂.

Thermochemical calculations

Both the enthalpy and entropy changes of the reactions were obtained using the second-law method. This procedure requires a knowledge of the rate constants as a function of temperature of both the forward and the reverse reaction. The Arrhenius expressions of the reverse reactions were either calculated from the ratios of the rate constants of $k(CH_3CI + Br)/k(C_2H_6 + Br)$ and $k(CH_3CH_2CI + Br)/k(C_2H_6 + Br)$ and the absolute rate constant of the reaction of C_2H_6 with Br or taken from literature.^{2,14-16}

Basically the second-law method uses the difference of the activation energies of both reaction directions to measure the enthalpy of reaction at the middle of the overlapping temperature, T_m , ranges on a 1/T scale of the forward and reverse reactions. The obtained ΔH° is then corrected to its room-temperature value using the heat capacities of the reaction species. At the same overlapping temperature the Gibbs energy change, ΔG° , is easily obtained from the ratio of the forward and the reverse rate constants. A simple relation between enthalpy and Gibbs energy makes it possible to calculate the entropy of the reaction at T_m which then is also corrected to the room-temperature value using the heat capacities of reactant species. $\Delta_f H^\circ_{298}$ of the radical is finally obtained from ΔH°_{298} and the tabulated heat of formation values of the other reaction species.

Chloromethyl radical

The Arrhenius expression for the reverse reaction was taken from the literature.¹⁴ This review article contains a critical evaluation of the work of Fettis, Knox and Trotman-Dickenson by Fettis and Knox. Fettis, Knox and Trotman-Dickenson studied a competitive bromination of methyl chloride-ethane mixture between the 332 and 473 K.²⁰ They stated that the only measurable products from the bromination reaction were ethyl bromide and bromochloromethane. The study produced the value of the ratio of the rate constants, which is used in the current study with the absolute rate constant of the reaction of Br atom with C_2H_6 molecule from a laser flash photolysis resonance-fluorescence investigation,² to calculate the absolute rate constant of the reaction (-1). The Arrhenius expression calculated is the following (in units of cm³ molecule⁻¹ s⁻¹): $k_{-1} = (1.3 \pm 0.6) \times 10^{-10}$ $\exp[-(57.7 \pm 2.3) \text{ kJ mol}^{-1}/RT]$. The ΔH° of the reaction was obtained at the mean temperature of the reaction directions directly from the difference of activation energies of the forward and reverse reactions: $\Delta H^{\circ}_{390} = E_a(1) - E_a(-1) =$ $-(53.6 \pm 2.3) \text{ kJ mol}^{-1}$.

The free energy change at 390 K was obtained from the thermodynamic equilibrium constant, $K_1 = k_1/k_{-1}$: $\Delta G_{390}^{\circ} = -RT \ln K_1 = -(29.1 \pm 1.4) \text{ kJ mol}^{-1}$.

The entropy change of the reaction was then calculated from the simple relation between ΔH° and ΔG° at the mean temperature: $\Delta S^{\circ}_{390} = (\Delta H^{\circ}_{390} - \Delta G^{\circ}_{390})/(390 \text{ K}) = -(62.7 \pm 6.9) \text{ J K}^{-1} \text{ mol}^{-1}$.

Finally the reaction enthalpy and entropy changes determined at 390 K were recalculated at 298 K by using tabulated heat capacities of the reactant species:^{21,22} $\Delta H_{298}^{\circ} = -(52.7 \pm 2.3) \text{ kJ mol}^{-1}$, $\Delta S_{298}^{\circ} = -(60.2 \pm 6.9) \text{ J K}^{-1} \text{ mol}^{-1}$.

The enthalpy of formation and entropy of CH_2Cl radical at room temperature were obtained from the reaction enthalpy and entropy changes at 298 K and the known heats of formation and entropy of other reaction species taken from the literature (see Table 2). The values obtained are as follows: $\Delta_f H_{298}^{\circ}(CH_2Cl) = 117.3 \pm 3.1 \text{ kJ mol}^{-1}$, $S_{298}^{\circ}(CH_2Cl) = 271 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$.

The experimental entropy value of CH₂Cl radical found in the current study is larger than the value of 243.37 J K⁻¹ mol⁻¹ obtained from a thermochemical database (see ref. 22). This calculated entropy value leads to a very different heat of formation value, 106.6 kJ mol⁻¹, of CH₂Cl radical in a thirdlaw calculation compared with the value of 117.3 kJ mol⁻¹ found by the second-law method in the current study. The Gibbs energy of reaction (1) at 298 K is calculated directly in the third-law procedure from the thermodynamic equilibrium constant value at the mean temperature: $\Delta G_{298}^{\circ}(CH_2Cl) =$ $-RT \ln K_{390} + \Delta S_{298}^{\circ}(390 - 298) - \Delta C_p^{\circ}(390 - 298) + \Delta C_p^{\circ}$ × 390 ln(390/298).

However, the accuracy of 106.6 kJ mol⁻¹ may not be good at all because the value means that the C—H bond strength of chloromethane has to be 408.3 kJ mol⁻¹ (see α -C—H bond strength of chloroethane later in this section). Also the value of 106.6 kJ mol⁻¹ means that the activation energy of Br + CH₃Cl reaction has a magnitude of 46 kJ mol⁻¹, which is almost the same as the activation energy of the reaction of CH₂Cl₂ with Br.

Dichloromethyl radical

The Arrhenius expression for the reverse reaction (-2) was taken from the most recent investigation.¹⁶ In this work Dymov and Tschuikow-Roux determined the rate constant of the CH₂Cl₂ + Br reaction to be (in units of cm³ molecule⁻¹ s⁻¹): $k_{-2} = (3.2 \pm 1.7) \times 10^{-11} \exp[-(47.0 \pm 2.5) \text{ kJ mol}^{-1}/RT]$ between 297 and 369 K. The mean temperature of the equilibrium reaction was found to be 433 K. At this temperature the following energy and entropy changes can be calculated: $\Delta H_{433}^{\circ} = -(37.2 \pm 2.7) \text{ kJ mol}^{-1}$, $\Delta G_{433}^{\circ} = -(21.6 \pm 1.6) \text{ kJ mol}^{-1}$, $\Delta S_{433}^{\circ} = -(36.1 \pm 7.3) \text{ J K}^{-1} \text{ mol}^{-1}$.

The reaction enthalpy and entropy changes were then recalculated at 298 K by using tabulated heat capacities of the reactant species.^{16,21} Typically values calculated differ only slightly from the values determined at $T_{\rm m}$: $\Delta H^{\circ}_{298} = -(36.2 \pm 2.7) \text{ kJ mol}^{-1}$, $\Delta S^{\circ}_{298} = -(33.3 \pm 7.3) \text{ J K}^{-1} \text{ mol}^{-1}$.

Finally, the enthalpy of formation and entropy of CHCl₂ radical at 298 K were obtained from the knowledge of the reaction enthalpy and entropy changes and the heats of formation and entropies of the other reaction species (see Table 2) at 298 K: $\Delta_{\rm r} H_{298}^{\circ}({\rm CHCl}_2) = 89.0 \pm 3.0$ kJ mol⁻¹, $S_{298}^{\circ}({\rm CHCl}_2) = 280 \pm 7$ J K⁻¹ mol⁻¹.

The most recent theoretical study of CHCl₂ radical is in ref. 16. There Dymov and Tschuikow-Roux used *ab initio* molecular orbital calculations to obtain an entropy for CHCl₂ radical of 280.66 J K⁻¹ mol⁻¹ at 298 K. This entropy value can be used in third-law calculations to obtain a value of 89.3 ± 2 kJ mol⁻¹ for the heat of formation of CHCl₂ radical. This value is practically the same as the one obtained by the second-law method in the current study.

 Table 2
 Heats of formation and entropies used in thermochemical calculations

species	$\Delta_{\rm f} H_{298}^{\circ}/{\rm kJ} {\rm mol}^{-1}$	$S_{298}^{\circ}/J \text{ K}^{-1} \text{ mol}^{-1}$
HBrª	- 36.44	198.70
Br ^a	111.86	175.02
CH ₃ Cl ^e	- 83.68	234.37
CH ₂ Cl ₂	-95.52	270.29
CH ¹ CH ¹ Cl ^b	-112.1	276.0
ĊH₃CHĈl₂'	-130.1	305.05

^a Data taken from ref. 21. ^b Data taken from ref. 30. ^c Data taken from ref. 25.

 Table 3
 Recommended heats of formation of radicals studied and C-H bond energies of corresponding hydrocarbons

R	$\frac{\Delta_{\rm f}H^{\circ}_{\rm 298}}{/\rm kJ\ mol^{-1}}$	$/J K^{S_{298}^{\circ}}_{mol^{-1}} mol^{-1}$	E _{d 298} /kJ mol ⁻¹
CH,Cl	117.3 ± 3.1	271 ± 7	419.0 ± 2.3
CHČI,	89.0 ± 3.0	280 ± 7	402.5 ± 2.7
CH ₃ CHCl	76.5 ± 1.6	279 ± 6	406.6 ± 1.5 ^a
CH ₄ CCl,	42.5 ± 1.7	288 ± 5	390.6 ± 1.5^{a}
CH,CIO,	-4 ± 11		
CHC1.0.	-17 + 7		

^a α -C-H bond energy.

a-Chloroethyl radical

The Arrhenius expression for the reverse reaction (-3) was calculated from the ratio of rate constants for $k(CH_3CH_2CI + Br)/k(C_2H_6 + Br)$ (the products of these bromination reactions were 1,1-bromochloroethane and ethyl bromide)⁴ and the absolute rate constant of the reaction of Br atom with ethane molecule studied by Seakins *et al.*² This simple calculation produced the following Arrhenius expression for reaction (-3) (units in cm³ molecule⁻¹ s⁻¹): $k_{-3} = (8.7 \pm 4.1) \times 10^{-12} \exp[-(37.8 \pm 1.5) \text{ kJ mol}^{-1}/RT]$ between 313 and 423 K. The mean temperature was found to be 360 K. At this temperature the following energy and entropy changes can be calculated: $\Delta H_{360}^{\circ} = -(40.7 \pm 1.5) \text{ kJ mol}^{-1}, \Delta G_{360}^{\circ} = -(30.7 \pm 1.3) \text{ kJ mol}^{-1}$. The meant

The reaction enthalpy and entropy changes were then recalculated at 298 K by using tabulated heat capacities for reactant species:^{21,23,24} $\Delta H_{298}^{\circ} = -(40.3 \pm 1.5)$ kJ mol⁻¹, $\Delta S_{298}^{\circ} = -(26.8 \pm 5.7)$ kJ mol⁻¹.

Finally the enthalpy of formation and entropy of CH₃CHCl radical were calculated at 298 K to be as follows (see Table 2): $\Delta_{f}H_{298}^{\circ}(CH_{3}CHCl) = 76.5 \pm 1.6 \text{ kJ mol}^{-1}$, $S_{298}^{\circ}(CH_{3}CHCl) = 279 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$.

In the third-law method a calculated value of 288.11 J K⁻¹ mol⁻¹ for CH₃CHCl radical obtained by Chen and Tschuikow-Roux²³ was used. This is translated to a value of (79.8 ± 1.7) kJ mol⁻¹ for the heat of formation of CH₃CHCl radical. Both the $\Delta_{\rm f} H_{298}^{\circ}$ values obtained by a second- or third-law procedures can be considered to be the same within their error limits.

a,a-Dichloroethyl radical

The values of thermochemical functions for CH₃CCl₂ radical were calculated in the same way as in the case of CHCl₂ radical. The Arrhenius expression for the reverse reaction (-4) was taken from the study of Dymov and Tschuikow-Roux.¹⁶ They determined it to be (units in cm³ molecule⁻¹ s⁻¹): $k_{-4} = (1.2 \pm 0.6) \times 10^{-12} \text{ exp}[-(30.9 \pm 1.4) \text{ kJ mol}^{-1}/$ *RT*] between 308 and 368 K. The mean temperature was found to be 443 K. At this temperature the following energy and entropy changes can be calculated: $\Delta H_{443}^{\circ} = -(25.0 \pm 1.5) \text{ kJ mol}^{-1}$, $\Delta G_{443}^{\circ} = -(21.2 \pm 1.5) \text{ kJ mol}^{-1}$, $\Delta S_{443}^{\circ} = -(8.5 \pm 4.9) \text{ J K}^{-1} \text{ mol}^{-1}$.

The reaction enthalpy and entropy changes were then recalculated at 298 K by using tabulated heat capacities for reactant species:^{21,23,25} $\Delta H_{298}^{\circ} = -(24.3 \pm 1.5)$ kJ mol⁻¹, $\Delta S_{298}^{\circ} = -(6.5 \pm 4.9)$ J K⁻¹ mol⁻¹.

The enthalpy of formation and entropy of CH₃CCl₂ radical at 298 K were obtained as (see Table 2): $\Delta_{f}H_{298}^{\circ}(CH_{3}CCl_{2}) = 42.5 \pm 1.7 \text{ kJ mol}^{-1}$, $S_{298}^{\circ}(CH_{3}CCl_{2}) = 288 \pm 5 \text{ J K}^{-1}$ mol.

The experimental entropy value of CH_3CCl_2 radical shown here is very much smaller than the calculated value of 314.55 J K^{-1} mol⁻¹ in ref. 23. This entropy value is translated in a third-law calculation to a value of 54.3 kJ mol⁻¹ for the heat of formation of the CH_3CCl_2 radical. This value is 11.8 kJ mol⁻¹ larger than the value of 42.5 kJ mol⁻¹ obtained by the second-law method shown above. However, there is reason to believe that the heat of formation value of 54.3 kJ mol⁻¹ is too large. This value means that the α -C—H bond in 1,1-dichloroethane should have a strength of 402.4 kJ mol⁻¹, which is practically the same as the C—H bond strength of dichloromethane found in the current study, or that the activation energy of the reaction of Br atom abstracting α -H from 1,1-dichloroethane equals a value of 42.7 kJ mol⁻¹. This also seems to be unlikely since the activation energy of the reaction of CH₃CH₂Cl + Br $\rightarrow \alpha$ -C₂H₄Cl + HBr is only 37.8 kJ mol⁻¹.

a-C-H bond energies

It is possible to calculate the R—H bond strength of the four chlorinated hydrocarbons from a knowledge of reaction enthalpy change of R + HBr \rightleftharpoons RH + Br equilibria and the bond strength of HBr. In practice the only error source in this case for the bond enthalpy is the accuracy of the determined reaction enthalpy change because the bond strength of HBr is known very precisely by spectroscopic studies. The bond enthalpy at 298 K is obtained simply using the following equation (see Table 3 for results): $E_{d \, 298} = -\Delta H_{298}^{\circ}(R + HBr \rightleftharpoons RH$ + Br) + $E_{d \, 298}(HBr)$.

Discussion

Rate constants of the $R + HBr (R = CH_2Cl, CHCl_2, CH_3CHCl or CH_3CCl_2)$ reaction

The measured R + HBr rate constants are displayed in Fig. 3 on an Arrhenius plot. As demonstrated in the figure the rate constants of $CH_2Cl + HBr$ reaction are higher than the rate constants of the reaction of $CHCl_2$ with HBr. A similar conclusion can be drawn on comparing the kinetics of the $CH_3CHCl + HBr$ reaction with the kinetics of the CH_3CCl_2 + HBr reaction: the CH_3CHCl radical reacts faster than CH_3CHCl_2 with HBr.

Only temperatures from 454 to 799 K were used to calculate thermochemical functions of $CHCl_2 + HBr$ reaction. Reaction (2) is expected to have a clearly positive temperature



Fig. 3 Arrhenius plot of radical + HBr reactions measured in the current study. The lines are Arrhenius expressions fitted to the rate constants, k_{1-4} .

dependence after comparing a set of halogenated methyl radical reactions with HBr.¹[†] Experiments below 454 K are most probably influenced by the inability of the apparatus to measure accurately small decays of a radical in the presence of a high concentration of HBr. At these low-temperature conditions heterogeneous wall-reactions of the radical are most likely to influence the observed kinetics. Besides, the reliably determined second-order rate constant, k, requires a wide concentration range of HBr to be used for the kinetics of radical + HBr reaction in order to measure the first-order rate constant values, k', which are up to 5 times (or more) larger than the first-order wall-loss process, k_7 , of the radical.

Reactivity of the radical

A possible reason for the reactivity of a polyatomic σ radical relies on its characteristic inductive effect, which can be considered to be a permanent polarization in the ground state of the radical, and is therefore manifested in its physical properties, such as dipole moment. A useful method of measuring inductive effects of radicals and to explain their reactivities by electronegativities is shown in ref. 26.

All of the radicals investigated in the current study are substituted by a Cl atom(s) and/or a methyl group directly to the centre carbon. From these two substituents, Cl atom has a tendency to draw electrons to itself thus lowering the electron density at the radical site. The phenomenon becomes stronger on increasing the number of Cl atoms substituted on the same carbon atom. On the other hand, a methyl group has the opposite influence compared with the Cl atom (or another halogen atom), releasing electrons toward the radical centre and thus increasing the reactivity of the radical. The radical + HBr reaction most likely proceeds through a loose intermediate complex,²⁷ where its stability depends on the dipole interaction between polarized reactants and/or on the interaction between the single occupied molecular orbital of the radical and the antibonding σ orbital of HBr. This interaction is increased by electron-donating groups and decreased by electron-withdrawing groups. From this theoretical point of view the kinetic results show expected trends determined by inductive effects in the reactivities of the radicals comparing sets of polyatomic free radical reactions with HI,²⁶ Cl₂ ²⁸ and Br₂.¹⁸

Traditional reactivity explanations

A classical way of explaining the reactivities of various free radicals by the exothermicity of their reactions does not apply here. For instance, by comparing reaction enthalpy changes of reactions (1) and (3) at 298 K one could expect a reverse order in reactivities of CH₂Cl and α -C₂H₄Cl radicals than is shown in Fig. 3. The reaction thermochemistry appears to play no role in determining the differences in reactivity among the reactions in the current study. The unimportance of the reaction thermochemistry in controlling radical reactivities is very well demonstrated by R + HI reactions in ref. 26.

Another method of explaining radical reactivities is to plot the rate constants of the radicals at a constant temperature against their ionization potential, E_i , value [or in general $\log(k_{R+X})$ vs. $(E_{i,R} - E_{ea,X})/(\alpha_R + \alpha_X)$, where $E_{ea,i}$ is electron affinity and α_i polarizability of compound i]. This has also been shown to be a poor method of explaining polyatomic free radical reactivities, see for instance ref. 28. In the current study this can not directly be tested for R + HBr reactions because the tabulated E_i values for CH₃CHCl and CH₃CCl₂ radicals are not available from the literature. However, an indirect comparison can be done between the reactivities of CH_2Cl and $CHCl_2$ radicals taken from the current study against the reactivities of alkyl radicals from ref. 2. A plot of the rate constants of these radicals against their E_i values shows no correlation.

Relative reactivities of the RH + Br reactions

The kinetics of the reverse reactions are shown in Fig. 4. The trend of the activation energies of these selective Br atom reactions is very obvious. The potential barrier in the reaction path of Br atom on abstracting the α -H atom from a molecule becomes smaller after the substitution of the H atom on the α -carbon by a methyl group and/or a Cl atom. The following trend in reactivities of the four Br atom reactions at 298 K per H atom can be found (normalized to the slowest reaction): 1485 $(CH_3CHCl_2) > 323$ $(CH_3CH_2Cl) > 29$ $(CH_2Cl_2) > 1$ (CH₃Cl). The reaction of CH₃CHCl₂ with Br is fastest and its activation energy is smallest of the four Br atom reactions. There are several possible factors to favour the radical formation at the transition state of reaction (-4). These include: (i) chlorine atoms stabilize the forming radical by drawing electrons from the centre carbon atom to themselves, (ii) the methyl group destabilizes the forming radical by acting as an electron donor but it also stabilizes the radical by a hyperconjugation effect and (iii) steric effects, which include the mutual repulsion of the nucleus and the bonding electrons of the chlorine atoms and the methyl group favour the formation of a planar sp² hybridized carbon atom. These three factors become less important when considering other three Br atom reactions.

Thermodynamic properties of the CH₂Cl radical

Andrews *et al.* have determined the adiabatic ionization energy of the CH₂Cl radical to be 8.75 eV from a photoelectron spectroscopic study.²⁹ This corresponds to $\Delta_f H_{298}^{\circ}(CH_2Cl)$ having a value of 115 kJ mol⁻¹ after calculation according the following equation:

$$\Delta_{\rm f} H^{\circ}(\rm CH_2 Cl) = \Delta_{\rm f} H^{\circ}(\rm CH_2 Cl^+) - E_{\rm i \ (adiabatic)} + \Delta_{\rm f} H^{\circ}(e^-)$$
(8)



Fig. 4 Arrhenius plot of the molecule + Br reactions used for the thermochemical calculations in the current study. The kinetics of the reactions shown are based on the Br atom abstracting the α -H atom in the molecules.

[†] The study of other halogenated methyl radical reactions with HBr as a function of temperature involving CH_2Br , CH_2I , CHBrCl and CCl_3 radicals will be published in due course.

where the heat of formation of the cation is taken to be 959 kJ mol⁻¹.³⁰ The calculated heat of formation of CH₂Cl is in good agreement with the value of 117.3 kJ mol⁻¹ obtained in the current study. The heat of formation of cation is not firmly established thus there is some uncertainty in the calculated $\Delta_{\rm f} H_{298}^{\circ}$ of the CH₂Cl radical.

Tschuikow-Roux and Paddison determined the heat of formation of the CH₂Cl radical to be 121.8 kJ mol⁻¹ from analysis of the bromination of chloromethane.31 For the reaction of CH₂Cl with HBr they estimated the activation energy to be 6.3 kJ mol⁻¹ from the trend of computed activation energies of various halogenated methanes. The value used by Tschuikow-Roux et al. is 2.2 kJ mol⁻¹ larger than the value measured in the current study. However, the activation energy, which they used for the $Br + CH_3Cl$ reaction, is 3.9 kJ mol⁻¹ larger also than the value used in the current study. The value used by Tschuikow-Roux et al. is based on a very complex reaction system where the Arrhenius expression for the reaction of CH₃Cl molecule with Br atom was obtained after using four different ratios of the rate constant values, and an experimentally determined Arrhenius expression for the reaction of $CF_3H + Br.^{32}$ In contrast, in the current study only one ratio of the rate constants and one time-resolved experimental rate constant are needed to obtain the Arrhenius expression for reaction (-1). One should also notice that Tschuikow-Roux et al. did not use any heat capacity corrections in their calculations to obtain the $\Delta_{f}H_{298}^{\circ}$ for the CH₂Cl radical. The total influence including the difference between the activation energies used by Tschuikow-Roux et al. and the current study (1.7 kJ mol⁻¹) and the heat capacity corrections $(0.8 \text{ kJ mol}^{-1})$ is 2.5 kJ mol⁻¹, which lowers the determination of Tschuikow-Roux et al. to a value of 119.3 kJ mol⁻¹. This value is inside the error limits of the current determination.

Holmes and Lossing determined $\Delta_r H_{298}^{\circ}$ of the CH₂Cl radical to be either 112.5 or 119.2 kJ mol⁻¹ depending the counter-ion used for the appearance energy measurements.³³ The method needs a knowledge of the heats of formation of the cation formed and the precursor. The values determined by the electron impact measurements including the error limits stated (± 8.4 kJ mol⁻¹) are in good agreement with the value determined in the current study.

DeCorpo et al. determined $\Delta_{\rm f} H_{298}^{\circ}$ of CH₂Cl radical to be as high as 125.5 kJ mol^{-1.34} The value was obtained from an appearance potential measurement of dichloromethane by using a time-of-flight mass spectrometer. The method used to determine the heat of formation value also requires a separate measurement to estimate the excess energy, such as the kinetic energy released in the process.

Thermodynamic properties of the CHCl₂ radical

Andrews *et al.* have determined the adiabatic ionization energy of the CHCl₂ radical to be 8.32 eV from photoelectron spectroscopic study.²⁹ This correspond to $\Delta_{f}H_{298}^{\circ}$ (CHCl₂) having a value of 84 kJ mol⁻¹. The heat of formation for the cation is taken to be 887 kJ mol⁻¹.³⁰ The heat of formation for the radical is 5 kJ mol⁻¹ lower than the value obtained in the current study. However, the accuracy of the heat of formation used for the cation is not well known,³⁰ this would also be reflected in some uncertainty in the calculated heat of formation value.

Benson and Weissman derived the heat of formation of $CHCl_2$ radical to be as high as 107.5 ± 4.2 kJ mol^{-1.35} They used a very complex reaction mechanism to analyse the pyrolysis of pentachloroethane. The product yields of the pyrolysis of C_2HCl_5 which included only a 6% reaction channel for producing the $CHCl_2$ radical were used to calculate the rate constants for all the initiation steps. These values and esti-

mated frequency factors of the reactions were used to determine the heat of formation for the CHCl₂ radical.

Tschuikow-Roux and Paddison determined the heat of formation of the CHCl₂ radical to be $98.3 \pm 5.0 \text{ kJ mol}^{-1.31}$ This value is based on the analysis of thermochemical and kinetic data on the bromination of dichloromethane. Tschuikow-Roux et al. estimated the activation energy of the $CHCl_2 + HBr$ reaction to be only 2.1 kJ mol⁻¹ from the trend of the computed activation energies of various halogenated methanes. This value is 7.7 kJ mol⁻¹ smaller than the activation energy determined directly in the current study. In addition, Tschuikow-Roux et al. did not use any heat capacity correction calculations to obtain their $\Delta_f H^\circ$ (CHCl₂) at 298 K. The total influence of these two estimates to the $\Delta_{\rm f} H_{298}^{\circ}$ of dichloromethyl radical is 8.7 kJ mol⁻¹, which is almost the same as the difference between the heat of formation values of 98.3 kJ mol⁻¹ as determined by Tschuikow-Roux and Paddison and that of 89.0 kJ mol⁻¹ found in the current study.

Thermodynamic properties of the CH₃CHCl radical

The heat of formation of the CH₃CHCl radical found in the current study is 76.5 kJ mol⁻¹. This value is larger than that determined by Miyokawa and Tschuikow-Roux (73.6 kJ mol⁻¹) from the photobromination of ethyl chloride.⁴ These workers measured the ratio of rate constants of the reactions of $CH_3CH_2Cl + Br$ and $C_2H_6 + Br$ and used it and the kinetics of the $C_2H_6 + Br$ reaction together with the estimated activation energy of reaction (3) to obtain the heat of formation for the CH₃CHCl radical. The individual Arrhenius expression for reaction (-3) was calculated by Miyokawa and Tschuikow-Roux using the ratio of rate constants determined by them and the rate constant of $C_2H_6 + Br$ reaction obtained from a very complex ratios of rate constants measurements.32 The small difference in the heat of formation determinations for CH₃CHCl radical, 2.9 kJ mol⁻¹, between the study of Miyokawa and Tschuikow-Roux and the current study can easily be covered by comparing the activation energies used for reaction (3) in the thermochemical calculations. In their investigation Miyokawa and Tschuikow-Roux used a value of +4.2 kJ mol⁻¹, whereas a measured value of -3.0 kJ mol⁻¹ was used in the current study. The difference between these two values increases the $\Delta_{\rm f} H_{298}^{\circ}$ of the CH₃CHCl radical by 7.2 kJ mol⁻¹ from the value of 73.6 kJ mol⁻¹. On the other hand, the activation energy of the $C_2H_6 + Br$ reaction determined by Amphlett and Whittle³² is as much as 3.9 kJ mol⁻¹ larger than the activation energy determined by Seakins et al. who used a time-resolved resonancefluorescence method in their investigations.² This difference has an opposite influence to the activation energy difference mentioned above for the thermochemistry of reaction (3). The final result of these corrections for $\Delta_{f}H^{\circ}_{298}$ of the CH_3CHCl radical is 76.9 kJ mol⁻¹ which is almost the same as the determined value in the current study.

Holmes *et al.* used an electron impact method to establish the heat of formation of the CH₃CHCl radical to be either 81.2 or 80.3 kJ mol⁻¹ depending on the counter-ion used for the appearance energy measurements.³³ The values obtained by Holmes *et al.* are in good agreement with the value determined in the current study when the large error limits (\pm 8.4 kJ mol⁻¹) of the appearance energy measurements are taken into consideration.

Thermodynamic properties of the CH₃CCl₂ radical

Chen and Tschuikow-Roux measured the heat of formation of the CH₃CCl₂ radical as 51.0 kJ mol⁻¹ by comparing a pair of competing atom-transfer reactions involving ethyl and α,α dichloroethyl radicals.²³ In their calculations for $\Delta_f H^{\circ}$ (CH₃CCl₂) using competing atom-transfer reactions they assumed the activation energies of both $C_2H_5 + HBr$ and $CH_3CCl_2 + HBr$ reactions to be equal. Both of these reactions have now been measured in the current study.¹ These new results demonstrate that the activation energy difference, $E_a(CH_3CCl_2 + HBr) - E_a(C_2H_5 + HBr)$, is actually 9.6 kJ mol⁻¹. Besides they used a value of 118.7 kJ mol⁻¹ for the heat of formation of the ethyl radical from the kinetic study of Pilling and co-workers³⁶ which later has been redetermined by them to be 120.2 kJ mol⁻¹.³⁷ The last determination is actually very close the value of 120.7 kJ mol⁻¹ demonstrated in ref. 1. The activation energy difference will reduce the value of $\Delta_f H_{298}^{\circ}$ (CH₃CCl₂) by 9.6 kJ mol⁻¹, the difference between the value used for $\Delta_f H_{298}^{\circ}$ (CH₃CCl₂) by 2.0 kJ mol⁻¹. The final value is then 43.4 kJ mol⁻¹, which is in good agreement with the current result (42.5 kJ mol⁻¹).

Chen and Tschuikow-Roux also calculated the heat of formation of CH_3CCl_2 radical to be 49.2 kJ mol⁻¹ on the basis of combining the *ab initio* calculated energy changes for homodesmic reaction with the known heats of formation of the other reaction components.²³ The reactants of the homodesmic reaction they used for the calculations are the CCl_3 radical and the CH_3CHCl_2 molecule. The method that they used to establish a semitheoretical value for the radical heat of formation can differ as much as 6.7 kJ mol⁻¹ from the experimental determination even though the reaction partners for the homodesmic reaction have been selected carefully. The inaccuracy of this estimation method is demonstrated in ref. 38 by the homodesmic reaction of $CH_3CHF_2 + CF_3 \rightarrow$ $CH_3CF_2 + CHF_3$.

α -C—H bond energies

Four different α -C-H bond energies were found in the current study. A trend of weakening α -C-H in hydrocarbons is very obvious. This phenomenon can easily be demonstrated after comparing the α -C-H bonds of C₁ and C₂ hydrocarbons separately in their own class. The bond strength is decreased in the case of substituted methanes in the following order: methane (437.9),† iodomethane (431),⁴⁰ bromomethane (427.4),¹ chloromethane (419.0), dichloromethane (402.5) and trichloromethane (393.9).[‡] Similarly the trend is demonstrated by substituted ethanes: ethane (422.6),¹ chloroethane (406.6) and 1,1-dichloroethane (390.6). The weakening of the C-H bond in both hydrocarbon classes can be explained by comparing the tendencies of halogen and H atoms to withdraw electrons from the C-H bond. From these two groups the halogen atom (in order Cl > Br > I) is more electronegative and thus has more negative inductive effect to the C-H bond than the H atom. Also other factors such as steric effects of substituents may influence the C-H bond strength (see Discussion). The increasing alkylation in hydrocarbons seems to be a reason to make the C-H bond weaker but this effect might be less important in the case of monohalogenated methanes.

Heat of formation of CHCl₂O₂ and CH₂ClO₂ radicals

The halogenated alkylperoxy radicals are difficult to detect by a mass spectrometric detection method. One reason for this is the very short lifetime of the generated alkylperoxy cations. However, it is possible to establish a heat of formation value for these very important free radicals from experimental investigations by detecting other species, such as R', of the alkylperoxy radical reaction. For instance, a study of the R' $+ O_2 \rightleftharpoons R'O_2$ equilibrium reaction yields the enthalpy of reaction. This value can then be used with the heat of formation of R' to calculate $\Delta_f H_{298}^\circ$ for R'O₂. Using this method one determines the heat of formation of CHCl₂O₂ to be -17 ± 7 kJ mol⁻¹ and of CH₂ClO₂ to be -4 ± 11 kJ mol⁻¹, respectively. The enthalpies of CHCl₂ + O₂ \rightleftharpoons CHCl₂O₂ and CH₂Cl + O₂ \rightleftharpoons CH₂ClO₂ equilibrium reactions were taken from literature.⁴²

This research was supported by the National Science Foundation, Chemistry Division, under Grant CHE-9102038 and by the Finnish Combustion Research Program LIEKKI. I thank Dr. Tschuikow-Roux for showing me the preliminary thermochemical and kinetic results of his and Dr. Dymov's investigations concerning the reactions of CH_2Cl_2 and CH_3CHCl_2 molecules with Br atom. I also thank Prof. Irene R. Slagle for kindly lending me the experimental apparatus used for this study.

Registry No. CH₂Cl, 6806-86-6; CHCl₂, 3474-12-2; CH₃CHCl, 16520-13-1; CH₃CCl₂, 19468-97-4; CH₂ClO₂, 73761-32-7; CHCl₂O₂, 73761-31-6; HBr, 10035-10-6; Br, 10097-32-2.

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[†] The reaction enthalpy of the $CH_3 + HCl \rightleftharpoons CH_4 + Cl$ equilibrium reaction taken from ref. 39 is used in the bond enthalpy calculation.

[‡] The bond dissociation energy was calculated from the following reaction: $CHCl_3 \rightarrow CCl_3 + H$. The $\Delta_r H_{298}^{\circ}$ values for $CHCl_3$,³⁰ CCl_3 ⁴¹ and H^{21} were taken from the literature.

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Paper 5/07698F; Received 27th November, 1995