Kinetics and thermochemistry of the R + HBr $\rightleftarrows$ RH + Br (R = C_2H_5 or β-C_2H_4Cl) equilibrium

An *ab initio* study of the bond energies in partly chlorinated ethanes and propanes

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The kinetics of the reaction of ethyl and β-chloroethyl radicals with HBr have been investigated under pseudo-first-order conditions in a heatable tubular reactor. The pressure-independent rate constants determined were fitted to the following Arrhenius expression (error limits stated are 1σ + Student's t values, units in cm^3 $molecule^{-1}$ s^{-1}): $k(C_2H_5) = (1.87 \pm 0.14) \times 10^{-12}$ $\exp[+(3.7 \pm 0.2)$ kJ $mol^{-1}/RT]$ and $k(\beta\text{-}C_2H_4Cl) = (5.7 \pm 1.6) \times 10^{-13}$ $\exp[+(2.2 \pm 0.8)$ kJ $mol^{-1}/RT]$. The kinetic data were used in a second-law procedure to calculate the entropy and enthalpy of formation values for the radicals studied at 298 K (entropy in J K^{-1} mol^{-1} and enthalpy in kJ mol^{-1}): 244 ± 6, 120.7 ± 2.1 (C_2H_5) and 271 ± 7, 93.0 ± 2.4 (β-C_2H_4Cl). The enthalpy of formation values of chloroethyl radicals were used in group additivity calculations to obtain $\Delta_f H^\circ_{298}$ values for six monochlorinated propyl and butyl radical isomers. Extensive *ab initio* molecular orbital calculations at the MP4/6-311G(d,p) level were used to determine all bond energies in monochlorinated ethane and propane, and in dichlorinated ethane molecules. The global minimum structures of open- and closed-shell species needed for calculations were determined at the MP2/6-31G(d,p) level. The calculated values are in close agreement with experimentally determined bond enthalpies. The calculations show a significant effect of chlorine atom(s) on the structure of chlorinated free radicals and on the bond energies of chlorinated molecules.

The role of chlorine as an atom, molecule or a part of an organic compound is central in combustion processes of chlorine-bearing polymeric materials. As an atom it has very high reactivity and a tendency to react with saturated hydrocarbons by a hydrogen atom abstraction reaction and with unsaturated hydrocarbons by a pressure-dependent addition reaction which, at elevated temperatures, becomes reversible (the abstraction channel then also becomes significant).[1,2] The abstraction reaction produces free radicals and HCl whereas the reaction with unsaturated hydrocarbons gives only free radicals at low temperatures. The resultant free radicals can react with molecular chlorine in exothermic reactions to produce molecular chlorides and Cl atoms.[3] Finally, the Cl atom attacks certain bonds preferentially. Typically, α-chlorinated alkyl radicals are formed as the principal products. The stability of these and other chlorinated alkyl radicals is largely influenced by intramolecular electronic effects and, hence, these free radicals will decompose unimolecularly to alkenes at different temperatures.

Until now bond energies of chlorinated saturated hydrocarbons have been determined experimentally using different spectroscopic or kinetic methods.[4–6] The halogen atom effect on the C—H bonds of molecules has been a subject for many studies of fluorocompounds[7–9] and some chlorocompounds.[10] However, in the case of chlorinated species such studies are restricted to the smallest compounds, where free radicals or cations formed during bond rupture processes are the most stable species containing only a few atoms. The present study combines experimental and computational techniques. A time-resolved kinetic technique being used to study the free radical kinetics with HBr and quantum chemical molecular orbital methods to determine the structures and energies of labile and stable species.

The chemical kinetics of ethyl and β-chloroethyl radicals with HBr have been studied, the latter having not been measured previously. The approach used was the same as that used for the study of chlorinated methyl and ethyl radical reactions with HBr.[5] The study was carried out to investigate the Cl atom effect on the radical reactivity and to obtain thermochemical properties of the free radicals for use in bond energy determinations. The *ab initio* calculations were then used to extend the bond enthalpy determinations to include monochlorinated propanes and dichlorinated ethanes, in order to investigate the influence of the Cl atom on the other bonds of the molecule. This information is useful in attempts to model large-scale combustion processes of chlorine-containing materials in which both oxidation and pyrolysis reactions of molecules and free radicals occur. All thermal molecular oxygen-free reactions will proceed through the most energetically favourable channels, which can be identified by studying the bond energies of the species involved.

Experimental study

Kinetic measurements

The rate constants for the reactions of ethyl and β-chloroethyl radical with HBr were studied as a function of temperature and pressure. The reactions were studied separately under pseudo-first-order conditions. The free radicals were photogenerated from suitable precursors inside a tubular flow reactor (see next section) and the kinetics of the reactions were followed by monitoring the decay of the radical as a function of time. Details of the experimental apparatus and conditions used have been described previously.[5,11–13] 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 Pyrex or quartz reactor. The 10.5 mm id reactor was coated with different materials (see Table 1). Gas flowing through the reactor at 5 m s^{-1} was completely replaced between laser pulses. The flowing gas contained the free radical precursor (typically <0.03%), HBr in varying concentrations and the carrier gas, He, in large

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Table 1 Measurement of the rate constants of the reaction R + HBr → RH + Br (R = C_2H_5 or β-C_2H_4Cl)

T[a]/K	[He]/10^{16} cm^{-3}	[HBr]/10^{13} cm^{-3}	k_3/s^{-1}	wall coating[b]	k_i[c]/10^{-12} cm^3 s^{-1}
$C_2H_5 + HBr \rightarrow C_2H_6 + Br$ (k_1)					
296	5.79	0.70–4.27	21	B_2O_3	8.47 ± 0.29
297	17.8	0.68–4.04	29	B_2O_3	8.59 ± 0.38
348	5.90	0.63–5.20	19	B_2O_3	6.80 ± 0.15
409	5.81	1.05–4.12	15	PDMS	5.71 ± 0.19
409	5.82	1.22–5.21	15	B_2O_3	5.52 ± 0.14
510	5.87	1.40–5.18	17	B_2O_3	4.41 ± 0.16
677	5.88	1.84–5.87	12	B_2O_3	3.70 ± 0.14
$k_1 = (1.87 \pm 0.14) \times 10^{-12} \exp[+(3.7 \pm 0.2)$ kJ mol$^{-1}/RT]$ cm^3 molecule^{-1} s^{-1}					
β-$C_2H_4Cl + HBr \rightarrow C_2H_5Cl + Br$ (k_2)					
300	17.7	7.58–22.7	50	HW	1.39 ± 0.22
300	5.79	5.07–18.6	37	HW	1.31 ± 0.08
300	17.7	8.71–21.3	31	HW	1.39 ± 0.06[d]
348	5.84	2.77–20.6	38	HW	1.25 ± 0.12
378	5.83	8.16–24.5	64	PDMS	1.04 ± 0.30
378	5.84	5.23–25.0	71	PDMS	1.12 ± 0.16
409	5.80	8.24–35.9	84	PDMS	1.13 ± 0.12
409	5.85	4.87–28.0	68	PDMS	1.04 ± 0.10
$k_2 = (5.7 \pm 1.6) \times 10^{-13} \exp[+(2.2 \pm 0.8)$ kJ mol$^{-1}/RT]$ cm^3 molecule^{-1} s^{-1}					

[a] Temperature uncertainty: ±2 K (296–378 K) and ± 3 K (409–677 K). [b] HW (halocarbon wax), PDMS [poly(dimethylsiloxane)] and B_2O_3. [c] Errors are 1σ + Student's t and based on statistical uncertainties. [d] CH_2BrCH_2Cl was used as a precursor.

excess (>99.5%). A portion of the gas mixture was sampled continuously through a 0.44 mm id hole located at the end of a nozzle in the wall of the reactor. A portion of the gas beam was photoionized by VUV light and the mass selected by a quadrupole mass filter in the vacuum chamber. Temporal ion signal profiles were recorded before and after the laser pulse with a multichannel scaler. Data were accumulated from 1000 to 20 000 repetitions of the experiments before being analysed by a non-linear least-squares analysis program.

The kinetics of the following metathetical reactions were studied:

$$C_2H_5 + HBr \rightarrow C_2H_6 + Br \quad (1)$$

$$\beta\text{-}C_2H_4Cl + HBr \rightarrow C_2H_5Cl + Br \quad (2)$$

The Arrhenius expressions of the forward reactions were combined with the Arrhenius expressions of the reverse, Br + RH, reactions[6,14] for the thermochemical calculations of the free radicals studied. Reaction (2) was studied over a narrower temperature range than reaction (1) since above 409 K the β-C_2H_4Cl radical starts to decompose unimolecularly. As expected the reactions did not show any pressure dependence at the gas densities used to study reactions (1) and (2). The results are listed in Table 1.

Photogeneration of radicals

The ethyl radical was generated by photolysis of ethyl iodide with radiation at 248 nm giving 3–4% photodissociation. The main photolysis channel is the rupture of the C—I bond. A minor channel is the production of $C_2H_4 + H + I$. This channel has also been observed by Brum *et al.* after photolysis of deuterium labelled iodoethanes at 248 nm in a time-of-flight mass spectrometer.[15] H atoms were monitored *via* two-photon ionization processes. It was concluded that H atoms were photogenerated almost exclusively by β-C—H bond scission.[15]

The β-chloroethyl radical was photogenerated either from CH_2BrCH_2Cl or CH_2ICH_2Cl. The latter being mainly used since it was easily photodissociated at 248 nm, giving a higher photolysis yield (4–6% *cf.* 1% for the bromocompound). However, the kinetic results with either precursor used under the same experimental conditions were identical (see Table 1), indicating that the excess internal energy formed during the photolysis did not have any measurable influence on the reaction kinetics. The main photolysis channel from both molecules is production of the β-chloroethyl radical and Br/I. The minor channel is the production of ethylene and halogen atoms.

The β-C_2H_4Cl radical starts to decompose above 409 K at the pressures used in the current study. At 510 K its half-life is <0.5 ms, whereas the half-life of its more stable isomer, α-C_2H_4Cl, is >60 ms.[5] At this temperature the ion signal of the β-isomer showed a clear first-order exponential decay without any displacement from the baseline, indicating isomerization to the α-C_2H_4Cl form. It was concluded that measurements at <410 K were not influenced by the isomerization process during the timescale of the study.

Rate constant data analysis

Experiments were conducted under pseudo-first-order conditions.[5] Only two radical reactions had significant rates under the conditions used for this study:

$$R + HBr \rightarrow RH + Br \quad (1)\text{ or }(2)$$

$$R \rightarrow \text{heterogeneous loss on the wall} \quad (3)$$

The initial radical concentrations were so low that radical–radical reactions had negligible rates compared with reactions (1)–(3). This was ensured by similar methods to those used previously.[5]

Bimolecular rate constants for reactions (1) and (2) were obtained from plots of the exponential radical decay constant k' *vs.* [HBr] {from $[R^+]_t = [R^+]_0 \exp[(-k't)$, where $k' = k_{1\text{ or }2}[HBr] + k_3$}. An example of an experiment to determine k_2 at one temperature is shown in Fig. 1. The temperature dependence of the rate constants is shown in Fig. 2.

Heterogeneous wall reactions

There exists a possibility that side reactions such as heterogeneous bimolecular reactions can occur in flow reactor experiments. This is especially true for experiments with HBr. The heterogeneous unimolecular reaction is taken into account in the data analysis (see above), but there is a possibility of a heterogeneous bimolecular reaction occurring between the reactants.[5] To minimize any influence of heterogeneous wall reactions, different coating materials were used (see Table 1). These coatings did not affect the value of the bimolecular R + HBr rate constant.

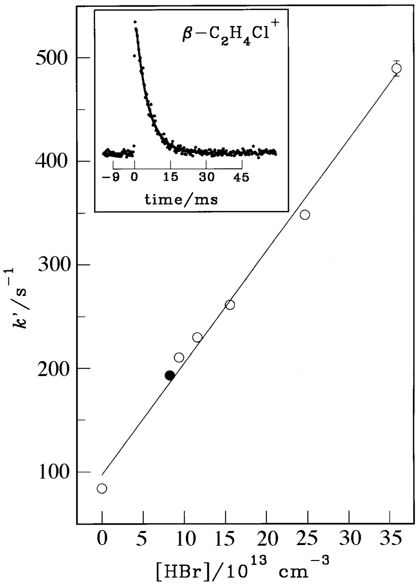

Fig. 1 First-order decay constant k' *vs.* [HBr] for one set of experiments conducted to measure the β-C_2H_4Cl + HBr rate constant, k_2, at 409 K. Insert is the ion signal profile of β-$C_2H_4Cl^+$ recorded during one of the experiments, shown as a solid circle in the linear regression fit. The line through the data in the insert is an exponential function fitted by a non-linear least-squares procedure. The first-order decay constant for β-$C_2H_4Cl^+$ in the displayed ion signal profile is (192.9 ± 4.0) s^{-1} ([HBr] = 8.24×10^{13} molecule cm^{-3}).

Accuracy of measurements

The error limits in the Arrhenius expressions are 1σ + Student's t and are based only on the statistical uncertainties. The reactions were studied under pseudo-first-order conditions and thus only the concentration of HBr needed to be known accurately. This was measured before and after the kinetic experiment and the mean value was used for the rate constant calculation (see more details in ref. 5). The other errors, including temperature and flow rate, were always <1% and were thus ignored.

Reagents

Helium (Matheson, 99.995%) was used without further purification. Hydrogen bromide (99%) and iodoethane (99%) were obtained from Aldrich, and 1-bromo-2-chloroethane (97%) and 1-iodo-2-chloroethane (97%) from Lancaster. The radical precursors were degassed by using freeze–pump–thaw cycles. HBr was collected in a flow trap kept at 77 K and was distilled several times under vacuum.[5]

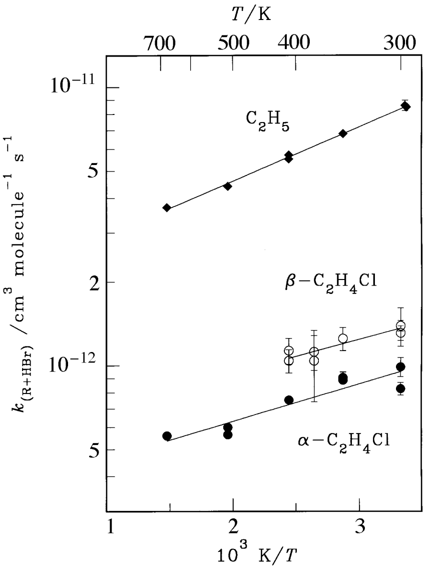

Fig. 2 Arrhenius plot of the radical + HBr reactions measured in the current study and in ref. 5 (α-C_2H_4Cl). The lines are Arrhenius expressions of the rate constants.

Photoionization

Reactants, free radicals and precursors were photoionized using atomic resonance radiation. An argon lamp (11.6, 11.8 eV) was used to ionize HBr, Br_2, Br, C_2H_4 and all the precursors. A hydrogen lamp (10.2 eV) was used to ionize CH_2CHCl and a chlorine lamp (8.9–9.1 eV) to ionize the free radicals.

Thermochemical calculations

Thermochemical functions for reactions (1) and (2) were obtained by a second-law method. The procedure is the same as that used previously.[5] Briefly, reaction enthalpy, entropy and free energy were calculated at the mean temperature, T_m, of both reaction directions. The reaction enthalpy change and entropy were then recalculated at room temperature using the heat capacities of the reaction species. Finally, the enthalpy of formation and the entropy of the free radical of interest were obtained using the ΔH° and ΔS° functions at 298 K and the tabulated $\Delta_f H^\circ_{298}$ and S°_{298}values of the other reaction species.

C_2H_5. The enthalpy of formation of the ethyl radical was determined to be 120.7 ± 2.1 kJ mol^{-1} using the second-law method. For comparison, the third-law method yielded $\Delta_f H^\circ_{298}(C_2H_5) = 122.7 \pm 2.4$ kJ mol^{-1}. The reverse reaction kinetics and thermochemical functions were taken from ref. 14 and Table 2. The results are shown in Table 3.

β-C_2H_4Cl. The Arrhenius expression for the reaction Br + $C_2H_5Cl \rightarrow$ HBr + β-C_2H_4Cl was determined to be $k_{-2} = (6.7 \pm 3.5) \times 10^{-12} \exp[-(55.3 \pm 2.3)$ kJ $mol^{-1}/RT]$ cm^3 $molecule^{-1}$ s^{-1} from 343 to 423 K. The kinetics of reaction (−2) were calculated from the ratio of rate constants:

Table 2 Enthalpies of formation and entropies used in thermochemical calculations

species	$\Delta_f H^\circ_{298}$ /kJ mol^{-1}	S°_{298} /J K^{-1} mol^{-1}
HBr[a]	−36.44	198.70
Br[a]	111.86	175.02
C_2H_6 [b]	−83.85	228.98
C_2H_5Cl[c]	−112.1	276.0
C_2H_5 [d]		246.8

[a] Data taken from ref. 16. [b] Enthalpy is taken from ref. 18 and entropy from ref. 17. [c] Enthalpy is taken from ref. 20 and entropy from ref. 21. [d] Entropy from ref. 19.

Table 3 Second-law determinations of $\Delta_f H^\circ_{298}$(R) and $E_{d\,298}$(R—H) based on the R + HBr $\rightleftarrows$ RH + Br equilibrium (R = C_2H_5 or β-C_2H_4Cl)

R	C_2H_5	β-C_2H_4Cl
T_m	537	373
$\Delta G^\circ_{T_m}$	−(35.4 ± 1.8)	−(49.8 ± 1.4)
$\Delta H^\circ_{T_m}$	−(57.0 ± 2.1)	−(57.5 ± 2.4)
$\Delta S^\circ_{T_m}$	−(40.2 ± 5.1)	−(20.6 ± 7.5)
ΔH°_{298}	−(56.3 ± 2.1)	−(56.8 ± 2.4)
ΔS°_{298}	−(38.4 ± 5.1)	−(18.6 ± 7.5)
$\Delta_f H^\circ_{298}$(R)	120.7 ± 2.1	93.0 ± 2.4
S°_{298}(R)	244 ± 6	271 ± 7
$E_{d\,298}$(R—H)	422.6 ± 2.1	423.1 ± 2.4

Energies and entropies in units kJ mol^{-1} and J K^{-1} mol^{-1}, and temperature in K.

Table 4 Calculated $\Delta_f H^\circ_{298}$ (in kJ mol^{-1}) of partly chlorinated propyl and butyl radical isomers

radical	$\Delta_f H^\circ_{298}$
$CH_3CH_2\dot{C}HCl$ (propyl, 1-chloro)	56.6 ± 3.4
$CH_3\dot{C}HCH_2Cl$ (ethyl, 2-chloro-1-methyl)	58.9 ± 3.8
$CH_3CH_2CH_2\dot{C}HCl$ (butyl, 1-chloro)	36.7 ± 3.4
$[CH_3]_2CH\dot{C}HCl$ (propyl, 1-chloro-2-methyl)	28.5 ± 3.4
$CH_3CH_2\dot{C}HCH_2Cl$ (propyl, 1-[chloromethyl])	39.0 ± 3.8
$[CH_3]_2\dot{C}CH_2Cl$ (ethyl, 2-chloro-1,1-dimethyl)	24.1 ± 3.4

$k(CH_3CH_2Cl + Br)/k(C_2H_6 + Br)$ as a function of temperature. Rate constants for the calculation were taken from ref. 14 and 6. The calculated thermochemical functions are shown in Table 3. Tabulated functions of the other reaction species were taken from ref. 16, 22, 23 and from Table 2.

The third-law procedure gives the heat of formation of β-C_2H_4Cl to be 97.5 ± 3 kJ mol^{-1} at 298 K. The entropy of the radical was found, using *ab initio* calculations, to be 282.9 kJ mol^{-1} at the MP2/6-31G(d,p) level of theory using a harmonic oscillator model (calculated frequencies were scaled by 0.9676 for the entropy calculation).[24] The third-law determination is in close agreement with the value of 93.0 ± 2.4 kJ mol^{-1} obtained by the second-law method.

Experimental C—H bond energies and group additivity

The C—H bond strengths in ethane and chloroethane were calculated directly from the reaction enthalpy changes according to: $E_{d,\,298} = -\Delta H^\circ_{298}(R + HBr \rightleftarrows RH + Br) + E_{d,\,298}(HBr)$. See Table 3 for results.

However, a group additivity method[22] was used to estimate the enthalpy of formation of monochlorinated propyl and butyl free radicals from the following principle:

$$\Delta_f H^\circ(\beta\text{-}C_2H_4Cl) + \Delta_f H^\circ(isoC_3H_7) = \Delta_f H^\circ(C_2H_5) + \Delta_f H^\circ(\beta,\ isoC_3H_6Cl)$$

The experimental $\Delta_f H^\circ_{298}$ values were taken from ref. 5 and 11 and from the current study. Calculated values are shown in Table 4. These values were needed to determine the experimental bond energies of some bulky chlorinated hydrocarbons, the results are shown in Table 5.

Table 5 Theoretically determined bond energies (in kJ mol^{-1}) of partly chlorinated ethanes and propanes

molecule	$E_{d\,298}$ calculated	$E_{d\,298}$ experimental	reference
$CH_3CH_2—H$	416.6	422.6 ± 2.1	this study
$CH_3—CH_3$	370.7	375.9 ± 1.4	[a]
$CH_2ClCH_2—H$	419.4	423.1 ± 2.4	this study
$CH_3CHCl—H$	405.2	406.6 ± 1.5	[b]
$CH_3CH_2—Cl$	340.3	354.1 ± 2.2	[a]
$CH_3—CH_2Cl$	375.4	375.4 ± 3.3	[a]
$CHCl_2CH_2—H$	424.6	n.a.	
$CH_3CCl_2—H$	397.8	390.6 ± 1.5	[b]
$CH_3CHCl—Cl$	324.5	327.9 ± 1.8	[a]
$CH_3—CHCl_2$	378.0	365.1 ± 3.3	[a]
$t\text{-}CH_2ClCHCl—H$	407.3	n.a.	
$CH_2ClCH_2—Cl$	338.9	345.1 ± 5.0	[a]
$CH_2Cl—CH_2Cl$	375.8	365.4 ± 6.2	[a]
$CH_3CH_2CH_2—H$	419.4	423.3 ± 2.1	[c]
$(CH_3)_2CH—H$	407.8	409.1 ± 2.0	[c]
$CH_3CH_2—CH_3$	371.5	371.2 ± 2.3	[a]
$CH_2ClCH_2CH_2—H$	418.7	n.a.	
$CH_2Cl(CH_3)CH—H$	406.5	409.3 ± 3.9	[a]
$CH_3CH_2CHCl—H$	407.0	407.0 ± 3.5	[a]
$CH_3CH_2CH_2—Cl$	345.3	354.5 ± 2.3	[a]
$CH_3—CH_2CH_2Cl$	376.5	371.4 ± 2.8	[a]
$CH_3CH_2—CH_2Cl$	378.2	370.4 ± 3.9	[a]
$CH_3CHClCH_2—H$	420.0	n.a.	
$(CH_3)_2CCl—H$	401.5	n.a.	
$(CH_3)_2CH—Cl$	347.8	352.9 ± 2.1	[a]
$CH_3—CHClCH_3$	376.3	367.5 ± 2.0	[a]

n.a. not available. [a] Enthalpy of formation values of species to calculate $E_{d\,298}$ (experimental) are from the current study, ref. 5, 11, 16 and 20. [b] Ref. 5. [c] Ref. 11.

Computational study

Computation details

Ab initio molecular orbital calculations were carried out with the GAUSSIAN 94 package of programs.[25] All calculations were carried out on an SGI Power Challenge computer at the Centre for Scientific Computing (Espoo, Finland). All geometries were fully optimized at the second-order Møller–Plesset perturbation theory using 6-31G(d,p) basis set and analytical gradient methods.[26] The optimized geometries of the species are the time independent, Born–Opperheimer structures and thus a possible internal rotor, such as the methyl group of the compound, may have different bond lengths and valence angles. For free radicals of interest, expectation values, S^2, were in the range 0.7500–0.7672, suggesting that there was only minor spin contamination. In principle, the frequency calculations were needed only to prove that the structure of the optimized compound was at the global minimum and to obtain the zero-point energy of the compound for calculations.

All energies of compounds were calculated at the MP4(SDTQ)/6-311G(d,p) level of theory. All zero-point energies were scaled by a factor of 0.9676 as suggested in ref. 24. The calculated bond dissociation energies were temperature corrected by $4RT$ where only translational and rotational contributions have been considered.[26] The bond energies were calculated directly from a homolytic bond dissociation reaction:

$$RX \rightarrow R + X$$

where X = H, Cl or free radical.

Optimized geometries

Geometries of open- and closed-shell molecules needed in the bond energy calculations represent the most stable conformer of each structural isomer. Frequency analyses were carried out at the MP2 level for all compounds.

Free radicals. The most stable rotameric structure for some free radicals was found to have no symmetry (C_1 point group, as a Schoenflies symbol) even though the isomeric structure of these species allows them to have one symmetry plane. Examples of this are the α-C_2H_4Cl, β,β-$C_2H_3Cl_2$ and α,n-C_3H_6Cl radicals.

The global minimum of the n-C_3H_7 radical has a different conformeric structure at the MP2 and HF levels. The HF optimized structure suggests that the H atoms at the radical site are in the same plane as the backbone, carbon skeleton, but in the Møller–Plesset optimized structure these H atoms are at an angle of ±81.3° to the backbone. However, the energy difference between these conformers is only 30 J mol^{-1} at the MP2 level.

The most stable conformer of α,β-$C_2H_3Cl_2$ is *gauche*. It is more stable than the *trans*-conformer by 6.41 kJ mol^{-1} at the MP2 level. Both rotamers belong to the C_1 point group, thus they have only an identity element. On the other hand for the molecule 1,2-dichloroethane, the *trans*-conformer (the chlorine atoms are antiperiplanar to each other) was found to be more stable than the *gauche*-conformer.

Table 6 Symmetry point groups, total and zero-point energies

compound	symmetry	total energy[a]	zero-point energy[b]	$\Delta_f H^\circ_{298}$[c] exp	ref.
H	K_h	−0.499 81	0.0	218.0	16
Cl	K_h	−459.602 63	0.0	121.3	16
CH_3	D_{3h}	−39.730 68	0.030 70	146.0	27, 28
CH_2Cl	C_s	−498.796 20	0.023 99	117.3	5
$CHCl_2$	C_s	−957.860 17	0.016 60	89.0	5
C_2H_5	C_s	−78.944 43	0.061 75	120.7	this study
β-C_2H_4Cl	C_s	−538.009 79	0.054 16	93.0	this study
α-C_2H_4Cl	C_1	−538.015 35	0.054 30	76.5	5
α,α-$C_2H_3Cl_2$	C_s	−997.082 15	0.045 91	42.5	5
α,β-$C_2H_3Cl_2$	C_1	−997.078 81	0.046 14		
β,β-$C_2H_3Cl_2$	C_1	−997.070 63	0.044 53		
n-C_3H_7	C_s	−118.156 36	0.091 74	100.8	11
α,*n*-C_3H_6Cl	C_1	−577.228 40	0.084 20		
β,*n*-C_3H_6Cl	C_1	−577.227 86	0.083 19		
γ,*n*-C_2H_6Cl	C_s	−577.222 93	0.083 17		
isoC_3H_7	C_s	−118.160 72	0.091 67	86.6	11
α,isoC_3H_6Cl	C_s	−577.235 44	0.083 74		
β,isoC_3H_6Cl	C_1	−577.228 20	0.083 80		
CH_3CH_3	D_{3d}	−79.614 33	0.077 46		
CH_2ClCH_3	C_s	−538.680 07	0.069 14		
$CHCl_2CH_3$	C_s	−997.743 07	0.059 73		
t-CH_2ClCH_2Cl	C_{2h}	−997.743 85	0.060 49		
$CH_3CH_2CH_3$	C_{2v}	−118.827 01	0.107 09		
$CH_2ClCH_2CH_3$	C_s	−577.893 35	0.098 58		
$CH_3CHClCH_3$	C_s	−577.898 32	0.098 14		

[a] In E_h, calculated at MP4/6-311G(d,p)//MP2/6-31G(d,p) level. [b] In E_h, unscaled value calculated at MP2/6-31G(d,p) level. [c] In kJ mol^{-1}.

Typically, the radical site of ethyl and *n*-propyl is at a small out-of-plane angle with the C_α—C_β bond leading to a pyramidal structure. The out-of-plane angle of all *n*-radicals (including α-radicals) increases as a function of Cl substitution, suggesting that an inductive effect controls the degree of non-planarity (see Table 7). However, the structure of the β,*n*-C_3H_6Cl radical is quite different from the other monochlorinated *n*-propyl radicals. In the β,*n*-C_3H_6Cl radical the dihedral angles of the H atoms at the radical site to the C_α—C_β—C_γ skeleton are at −160.1° and 37.3°. The proximity of a large Cl atom at C_β and the presence of C_γ forces the H_α atoms to become almost parallel to the backbone of the radical (a similar structural form was also calculated for β,*n*-C_4H_8Cl). In the β-C_2H_4Cl radical the H_α atoms are also located on both sides of the Cl atom when observed along the C_α—C_β bond but the radical site is not twisted because the Cl atom is at the symmetry plane of the radical. For the β,*n*-C_3H_6Cl (or β,*n*-C_4H_8Cl) radical a similar kind of symmetry operator cannot be placed.

For isopropyl radicals the out-of-plane angle is largest for those isomers where the Cl atom is at the radical centre. This observed non-planarity parallels that for the *n*-type radicals.

For all chlorinated radicals the C—Cl bond length is shortest when the Cl atom is at C_α and longest when it is at C_β. The same trend can be found for the C—H bonds in ethyl and *n*-propyl. Generally, a similar trend can also be observed for chlorinated radicals but the Cl atom seems to confuse this trend by having a tendency to shrink the C—H bond connected at the same carbon atom. Furthermore, the C—C bonds seem to follow the same trend in that the C_α—C_β is the shortest bond. Generally speaking, the Cl atom has a tendency to make the Cl—C—H angle smaller than the H—C—H angle for methylene carbons and for radical centres. Tables listing the structural parameters of the free radicals have been deposited with the British library.‡

Table 7 Out-of-plane angles (in degrees) of the radicals at MP2/6-31G(d,p) level

C_2H_5	12.8
α-C_2H_4Cl	22.8
β-C_2H_4Cl	14.6
α,α-$C_2H_3Cl_2$	29.8
α,β-$C_2H_3Cl_2$	19.2
β,β-$C_2H_3Cl_2$	14.5
n-C_3H_7	14.7
α,*n*-C_3H_6Cl	23.4
β,*n*-C_3H_6Cl	345.0
γ,*n*-C_3H_6Cl	10.3
isoC_3H_7	19.2
α-isoC_3H_6Cl	28.8
β-isoC_3H_6Cl	18.7

Molecules. The point groups of molecules are given in Table 6. A table listing the geometric parameters of the molecules has been deposited with the British Library.‡

In general, the C—Cl bond is shorter in a CH_2Cl group than in a CHCl group. As for the radicals, the Cl atom makes the nearest C—C bond the shortest of the C—C bonds in the molecules and the H—C—Cl bond angle is smaller than the H—C—H bond angle.

Discussion

Kinetics of R + HBr

The measured rate constants for the reactions of ethyl and β-chloroethyl radical with HBr are displayed in Fig. 2 on an Arrhenius plot together, for comparison, with the rate constants of the α-chloroethyl + HBr reaction (taken from ref. 5). The kinetics of the ethyl + HBr reaction measured in the current study agree well with those found previously.[14] It can be seen from Fig. 2 that both chlorinated ethyl radicals are less reactive than the ethyl radical with HBr. Furthermore, β-C_2H_4Cl reacts faster than its more stable isomer.

A possible reason for the decreasing reactivity on chlorine atom substitution may be the difference in atom electronegativities between Cl and H atoms. The Cl atom is more electronegative than the H atom and thus has a stronger tendency to draw electrons from the radical centre. This phenomenon is strongest at the α-position and weaker at the β-position

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‡ Available as supplementary material (**SUP 57342**; 5 pp.) deposited with the British Library. Details are available from the Editorial Office.

because of the distance from the radical centre. Thus it is obvious that the electron-withdrawing tendency of Cl atom(s) from the radical centre becomes weaker in the following order: α,α-$C_2H_3Cl_2$ > α-C_2H_4Cl > β-C_2H_4Cl > C_2H_5.[5] The reverse trend is found for the reactivities of these radicals. Similarly, the reactivity increases from chlorinated to non-chlorinated radicals for methyl radicals: $CHCl_2 < CH_2Cl < CH_3$.[5,14] Both trends can also be seen after comparing the calculated atomic spin densities of the free radicals. For every free radical studied the calculated spin density is highest at the C_α atom, a clear indication that the unpaired electron is located at the radical site.

Stability of chlorinated free radicals

The chlorine atom, as a substituent on the radical skeleton, also has an interesting tendency to either increase or decrease the thermal stability of the radical. The effect is mediated by the position of the Cl atom on the radical skeleton. At the α-position the Cl atom increases the thermal stability. This is demonstrated for the ethyl and α-chlorinated ethyl radicals where the α,α-dichloroethyl radical is the most stable.[5] At the β-position the Cl atom reduces the thermal stability of the radical. A possible explanation is the negative inductive effect of the Cl atom. The effect is stronger for the α-isomer than for the β-isomer because the electron-withdrawing effect of the Cl atom from the radical centre changes as a function of distance. For chloroethyl radicals the β-isomer starts to decompose at 410 K (see Fig. 2). For the same reason the thermal stability of CCl_3CH_2 is low. It starts to decompose unimolecularly by C—Cl bond rupture at *ca.* 450 K at a few torr of pressure.

Free radical stabilities can also be considered theoretically by comparing the calculated energies of the most stable conformers from *ab initio* calculations. However, the comparisons are then limited to compounds containing equal numbers of the same atoms. As a result the calculations show that the α-chloroethyl radical is *ca.* 14.2 kJ mol^{-1} more stable than the β-chloroethyl radical at 0 K at the MP4/6-311G(d,p) level of theory (zero-point energy corrected values considered). The calculations suggest the following stability order for dichloroethyl radicals: α,α-$C_2H_3Cl_2$ > α,β-$C_2H_3Cl_2$ > β,β-$C_2H_3Cl_2$, the same trend as for the monochloroethyl radicals (see Table 5). The comparisons can also be extended to include the propyl radicals studied here. The results from the calculations suggest the following stability trend $\alpha > \beta > \gamma$ and secondary > primary (the zero-point energy corrected MP4 energies are compared). The only exception to these trends is found for α- and β-chloro-*n*-propyl radicals. According to calculations the β-form is more stable by *ca.* 1.1 kJ mol^{-1} at 0 K. The α-form has a larger zero-point energy correction, causing it to be less stable than the β-form. Traditionally, the thermal stabilities (or stabilities in general) of carbon centred σ free radicals have been explained by comparing C—H bond strengths of analogous hydrocarbons. This type of consideration is misleading and should not be used, as explained in ref. 11.

Thermodynamic properties of the C_2H_5 radical

The enthalpy of formation of the ethyl radical was found to be 120.7 ± 2.1 kJ mol^{-1}, in excellent agreement with the most recent experimental time-resolved study[29] and with the theoretically determined value of Bauschlicher Jr. and Partridge.[30] They determined the C—H bond energy in ethane directly by using coupled cluster and perturbation theory calculations with large basis sets. The authors concluded that the C—H bond energy is 417.5 kJ mol^{-1} at 0 K, which can be temperature corrected to 422.9(±2.1) kJ mol^{-1} using an integrated heat capacity correction. The bond energy can be translated to ΔH°_{298} (C_2H_5), giving a value of 121.1 ± 2.1 kJ mol^{-1}.

Thermodynamic properties of the β-chloroethyl radical

Miyokawa and Tschuikow-Roux determined the enthalpy of formation of the β-C_2H_4Cl radical to be 91.2 ± 4.1 kJ mol^{-1},[6] close to the value determined in the current study. However, the agreement is misleading. Miyokawa and Tschuikow-Roux used a gas-phase photobromination of ethyl chloride in the range 343–423 K, where the abstraction of α-H atom is in competition with the β-H atom abstraction reaction. They calculated the individual Arrhenius expression for reaction (−2) using the ratio of rate constants determined by them and the rate constant of the C_2H_6 + Br reaction obtained from very complex ratios of rate constant measurement.[31] The kinetics of this reaction have recently been remeasured by a time-resolved resonance-fluorescence technique and the activation energy of the reaction was found to be *ca.* 4 kJ mol^{-1} smaller.[14] In addition Miyokawa and Tschuikow-Roux estimated the activation energy of the C_2H_5 + HBr reaction from thermochemical calculations. This value has also been measured directly by time-resolved techniques earlier and in the current study, and was shown to be *ca.* 5 kJ mol^{-1} smaller than the estimated value used in ref. 6. The errors in the activation energies fortuitously cancel each other.

An electron impact method has been used to determine $\Delta_f H^\circ_{298}$(β-C_2H_4Cl) to be 95.4 ± 8.4 kJ mol^{-1}, an average value from two different determinations.[32]

Trends in bond energies

Chlorinated compounds have been little studied by *ab initio* MO calculations. A reason for this might be the presence of Cl atom(s) which make higher level calculations time consuming. Some chlorinated C_1 compounds[33] have been optimized at the MP2 level but larger molecules[34] and free radicals[23] have been studied only at the Hartree-Fock level.

The main reason for carrying out numerous *ab initio* calculations at the MP2 and MP4 levels was to investigate the influence of different substituents on the C—H bond energies in partly chlorinated saturated hydrocarbons. These have not been studied previously by quantum chemical calculation. Particular consideration was given to the effect of the Cl atom on its neighbouring C—H bond strengths. All the calculations were carried out at the same level of theory and thus the relative calculated energies of the compounds are accurate and, furthermore direct and reliable bond energy determinations can be performed. The calculated bond strengths are shown in Fig. 3 and comparisons with experimental values are given in Table 5.

In general, the weakest bond in the chlorinated molecules studied is found always to be a C—Cl bond. The strongest

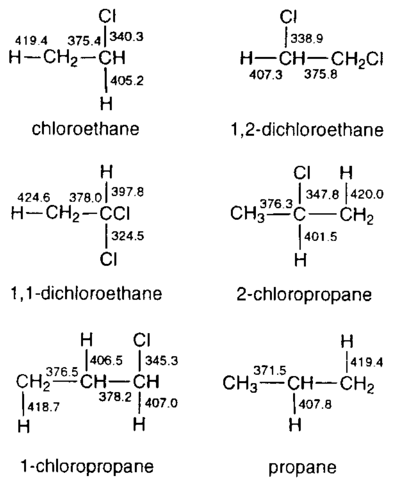

Fig. 3 *Ab initio* calculated bond strengths (in kJ mol^{-1}) of partly chlorinated hydrocarbons

bond is the C—H bond. The same can be concluded from experimental investigations (see Table 5 and ref. 11).

C—H bonds. The influence of the Cl atom on the C—H bonds of chlorinated molecules is surprisingly obvious. The experimental studies have already proved the α-C—H bond to be much weaker than the β-C—H bond in chloroethane and 1,1-dichloroethane,[5] a fact which was confirmed by *ab initio* calculations here. Typically, a primary C—H bond has a strength of 420 kJ mol^{-1} when the carbon atom of this bond is not bonded to a Cl atom. However, this bond strength is decreased by 13 kJ mol^{-1} if the Cl atom is also connected to the primary carbon. On the other hand a secondary C—H is weakened only by 6 kJ mol^{-1} by the presence of a Cl atom. The clear influence of the Cl atom seems to extend only to the neighbouring bonds (C_β—H).§ On the other hand, if the C_β—H bond is the primary bond, as in ethanes, Cl atom(s) makes it stronger.

C—C bonds. The influence of the Cl atom on the other bonds of the molecule seems to be most marked for C—H bonds. Calculations do not show any similar phenomenon for C—C bonds of chlorinated compounds, in fact the C—C bond strengths seem to decrease slightly when they are removed further from the influence of the Cl substituent.§ The weaker influence of the Cl atom on the C—C bond than on the C—H bond may be explained by considering the atom electronegativities of these elements. The Cl atom is the most negative and the H atom is the least negative, thus one may expect the Cl atom to have a stronger influence on the partly ionic C—H bond than on the covalent C—C bond. As a consequence of this negative inductive effect the electron density above and below the nodal plane of the bond is polarized toward the Cl atom.

C—Cl bonds. The calculated C—Cl bond strengths of monochloro compounds seem to be in the range 339–350 kJ mol^{-1}, where the C—Cl bond strength increases with the size of the molecule.§ Only the C—Cl bond in 1,1-dichloroethane is clearly below these values. The neighbouring Cl atom most likely causes this. The same can be concluded from a comparison of the C—Cl bond in chlorinated methanes. The C—Cl bond becomes weaker in the following order (in kJ mol^{-1}): 351.0 (CH_3Cl) > 334.1 (CH_2Cl_2) > 315.1 ($CHCl_3$) > 288.3 (CCl_4).[5,35]

Accuracy of calculated bond energies

The accuracy of the calculated bond energies can be compared with the experimental values shown in Table 5. Typically, the calculated C—H bond energies are 2–6 kJ mol^{-1} lower than the experimentally determined values.[5,11] The difference is only 1–2 kJ mol^{-1} for secondary and α-C—H bonds and 4–6 kJ mol^{-1} for primary C—H bonds of non-chlorinated molecules. This difference seems to be systematic. However, the calculated α-C—H bond strength of 1,1-dichloroethane clearly differs from the experimental value (390.6 kJ mol^{-1}),[5] the calculated value being 7.2 kJ mol^{-1} larger. On the other hand, the results from the third-law method indicate that the α-C—H bond strength is as high as 402.4 kJ mol^{-1}.[5] However, this value seems to be too large, as discussed in detail previously.[5] The correct value could be *ca.* 395 kJ mol^{-1}, after considering the activation energies of the bromination reactions of chloroethane and 1,1-dichloroethane.[5] This increases $\Delta_f H^\circ_{298}$ (CH_3CCl_2) to 47 kJ mol^{-1}.

The difference between calculated and experimental C—C bond energies are typically 1–5 kJ mol^{-1} for non-chlorinated hydrocarbons and 4–14 kJ mol^{-1} for chlorinated hydrocarbons. However, comparisons with chlorinated molecules is difficult because of the absence of experimentally determined enthalpy of formation values for chlorinated polyatomic free radicals.

For C—Cl bond energies the difference between calculated and experimental values is ± 13 kJ mol^{-1}. However, in some cases tabulated $\Delta_f H^\circ_{298}$ values of chlorinated molecules have error limits as large as ± 8 kJ mol^{-1}.

All calculated bond energies shown in the current study are determined such that the most stable conformeric species of the dissociation reaction are considered. This is not the case for the experimental determination. Typically, the enthalpy of formation has been determined for a molecule consisting of a mixture of different stereoisomers in accordance to the Boltzmann distribution. The enthalpy of formation of different conformers of the molecule can differ significantly. For example, different C—H bond energies of 1,2-dichloroethane can be calculated by the *ab initio* method if the molecule is considered to be either the *trans*- or *gauche*-isomer. The latter is the less stable isomer and leads to a 6.1 kJ mol^{-1} weaker C—H bond strength than the former.

Conclusion

The chlorine atom effect on the structures and bond energies of partly chlorinated ethanes and propanes has been demonstrated by experimental and theoretical investigations. Rather straightforward *ab initio* calculations at MP2/6-31G(d,p) //MP4 (SDTQ) /6-311G(d,p) level seem to be adequate to show the importance of the electronic effects of a chlorine atom on the structure of the molecule. There is good agreement between the calculated and the experimental bond energies of the compounds studied. The effect of the chlorine atom on the reactivity and the thermal stability of the radical is also shown by experimental kinetic studies.

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