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Heats of Formation and Bond Dissociation Energies in Halogen-Substituted Methyl and Ethyl Radicals

John L. Holmes* and F. P. Lossing

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Abstract: Heats of formation of halogen-substituted methyl and ethyl radicals have been measured by monoenergetic electron impact on selected precursor molecules as follows: CH_2Cl 27.7, $CHCl_2$ 22.3, CCl_3 18.0, CH_2Br 40.2, $CHBr_2$ 44.4, CBr_3 49.0, CH_2I 54.9; $ClCH_2CH_2$ 22.8, $ClCHCH_3$ 19.3, $BrCH_2CH_2$ 32.3, and $BrCHCH_3$ 27.3 (all values ±2, in kcal mol^{-1}).

Tschuikow-Roux and his co-workers have recently reported[1,2] heats of formation, ΔH_f°, of a series of halogenated methyl and ethyl radicals. Their method involved the determination of Arrhenius activation energies for competitive halogenation reactions.

The use of appearance energies, AE, for ionic dissociations

$$RY + e \rightarrow Y^+ + R^\bullet + 2e$$

in which simple free radicals, $[R^\bullet]$, are the neutral fragment, has been shown by ourselves to yield ΔH_f° values in good agreement with those obtained via conventional kinetic measurements.[3]

$$AE = \Delta H_r = \Delta H_f^\circ[Y^+] + \Delta H_f^\circ[R^\bullet] - \Delta H_f^\circ[RY]$$

This approach is possible because ΔH_f° values for many organic cations are now at least as well established as those for many neutral species.[4] An advantage of the AE method is that only one reaction is involved, and complications from bimolecular processes are avoided. The necessary criteria for the success of such experiments are outlined below.

1. The AE for the counterion, $[Y^+]$, must be measured by a high-energy resolution method (photoionization, photoionization photoelectron coincidence, or electron monochromator) with at least unit mass resolution and long observation times (i.e., ion lifetimes to collection $\geqslant 10^{-5}$ s).

2. A suitable dissociation reaction must be selected. All neutral heats of formation must be available or capable of accurate estimation. Preferably, the dissociation reaction should be mechanistically simple, such as a single bond cleavage or a molecular elimination involving a six-centered transition state (e.g., McLafferty rearrangement), and should also be the fragmentation of lowest energy requirement. The latter condition is necessary because the AE values for reactions of higher energy requirements tend to be high because of kinetic competition from lower energy processes.

3. If the reaction produces a metastable peak, then the kinetic energy release characteristics of the process should be examined.[5] If the average released kinetic energy is very small (ca. 0.5 kcal mol^{-1}), then it reasonably may be assumed that the fragmentation proceeds at or very close to the thermochemical threshold. However, if the average kinetic energy release exceeds ca. 2 kcal mol^{-1} (simple Gaussian-type metastable peak), or if the metastable peak is of composite shape, then the measured AE may contain an indeterminate excess energy term and the derived ΔH_f° of the daughter ion will be a maximum value. In these cases, only if the ion internal energy for the metastably dissociating species and the corresponding kinetic energy release distribution are both accurately known can any valid correction be applied. Complications associated with kinetic energy release were not encountered in the present work.

We have chosen the counterion Y^+ with these points in view; in most cases it was the base peak in the normal mass spectrum of the precursor.

In the present work, we have applied this method to measure heats of formation of halogen-substituted methyl and ethyl free radicals, in order to establish the stabilizing effects of different halogen atoms and of their position relative to the free electron center.

Experimental Section

Thresholds for the ionic dissociations were measured by impact of an energy-selected electron beam from an electrostatic electron monochromator. This apparatus and the experimental procedures have been described.[6] The appearance energy for the formation of Y^+ was determined from the onset of ion current at the appropriate mass, as the energy of the electron beam was increased by 0.02-eV steps. The energy scale was calibrated against the ionization energy of H_2O which was admitted simultaneously.

Results and Discussion

Halomethyl Radicals. Table I shows the collected results for the halomethyl radicals. The estimated uncertainty in the new heats of formation is ±2 kcal mol^{-1}, part of which arises from the use of additivity to estimate some $\Delta H_f[RY]$ values. With one exception the ΔH_f°[radical] values are in very good agreement with literature values,[8] some of which are as much as 30 years old. Recent high-level ab initio molecular orbital theory calculations on the $CH_2Cl^\bullet$, $CHCl_2^\bullet$, and $CCl_3^\bullet$ radicals[9] gave values in good agreement with experiment (Table I).

Single halogen substitution has the effect of lowering $D(CH_2X-H)$ by 4, 3.5, and 1 kcal mol^{-1} for X = Cl, Br, and I, respectively. Multiple substitution by Cl gives an additional decrease of 2 kcal mol^{-1} per Cl atom in the bond strength. For bromine the effect to CBr_3-H is similar. For $D(CHBr_2-H)$ there is some uncertainty arising from the value of $\Delta H_f^\circ(CH_2Br_2)$. Values listed in the review of McMillen and Golden[8] for $D(CBr_3-H)$ = 103.7 kcal mol^{-1} and $\Delta H_f^\circ(CHBr_2)$ = 54.3 kcal mol^{-1} correspond to $\Delta H_f^\circ(CH_2Br_2)$ = +2.7 kcal mol^{-1}. A new compilation[4] gives −2.7 kcal mol^{-1}. Neither of these values seems consistent with $\Delta H_f^\circ(CH_3Br)$ = −8.5 kcal mol^{-1} [10] and $\Delta H_f^\circ(CHBr_3)$ = 5.7 kcal mol^{-1}.[4] We have adopted the value

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Table I. Appearance Energies, Heats of Formation, and *D*(R–H) for Halomethyl Radicals (AE Values in eV ± 0.05, $\Delta H_f°$ and *D*(R–H) in kcal mol^{-1})

radical [R•]	counterion [Y^+]	$\Delta H_f°[Y^+]$[a]	$\Delta H_f°$[RY][b]	AE[Y^+]	$\Delta H_f°$ [radical][R•]		$\Delta H_f°$[RH]	*D*(R–H)[g]
					this work	lit.		
CH_2Cl	CH_2OH	169	−61.5	11.16	26.9	28.3[c]		
	$C(CH_3)_3$	166	−45.3	10.40	28.5	29.1[d]		
					av 27.7	28.6[e]	−19.6[f]	99.4
$CHCl_2$	CH_2OH	169	−64.9	11.08	22.3	24.1[c]		
	$COCH_3$	156	−57.0	10.20	22.2	23.3[e]		
					av 22.3		−22.8[f]	97.2
CCl_3	CH_2OH	169	−66.7	11.00	18.0	19 ± 1[c]	−24.8[f]	94.9
						17.9[e]		
CH_2Br	CH_2OH	169	−51.8	11.34	40.7	41.5[c]		
	CH_3CHOH	139	−60.0	10.34	39.5	40.3[d]		
	COOH	141	−98	12.12	40.4			
					av 40.2		−8.5	100.8
$CHBr_2$	CH_2OH	169	−44	11.16	44.4	54.3[c]	−1.4[h]	97.9
CBr_3	CH_2OH	169	−38.5	11.10	49.0	49.6[c]	5.7[a]	95.4
CH_2I	CH_2OH	169	−38.1	11.36	54.9	55.0[c]	3.5[f]	103.5

[a] Reference 4. [b] Calculated using the additivity scheme of Benson;[7] see also Table II. [c] Reference 8. [d] Reference 1. [e] From ab initio molecular orbital theory calculations, ref 9. [f] Reference 10. [g] Compare $D(CH_3–H)$ = 104.3 kcal mol^{-1},[11] *D*(R–H) values from this work. [h] See text.

Table II. Appearance Energies, Heats of Formation, and *D*(R–H) for Haloethyl Radicals (AE Values in eV ± 0.05, $\Delta H_f°$ and *D*(R–H) in kcal mol^{-1})

radical [R•]	counterion [Y^+]	$\Delta H_f°[Y^+]$[a]	$\Delta H_f°$[RY]	AE[Y^+]	$\Delta H_f°$ [radical][R•]		$\Delta H_f°$[RH][b]	*D*(R–H)[j]
					this work	lit.		
$ClCH_2\dot{C}H_2$	$COCH_3$	156	−62[c]	10.42	22.3			
	CH_2OH	169	−66[c]	11.20	23.3			
					av 22.8		−26.8	101.7
$Cl\dot{C}HCH_3$	$COCH_3$	156	−58[d]	10.12	19.4	16.8[h]		
	CH_2OH	169	−69.9[e]	11.19	19.2			
					av 19.3		−26.8	98.2
$BrCH_2\dot{C}H_2$	COOH	141	−102.9[f]	11.92	31.0			
	CH_2OH	169	−55.5[f]	11.18	33.3			
					av 32.3		−14.8	99.2
$Br\dot{C}HCH_3$	COOH	141	−104.2[g]	11.82	27.4	29.6[i]		
	$COCH_3$	156	−52.6[g]	10.22	27.1			
					av 27.3		−14.8	94.2

[a] Reference 4. [b] Reference 10. [c] By additivity[7] and using $C–(Cl)(C)(H_2)$ = 15.1 kcal mol^{-1} from data in ref 10. [d] By additivity[7] and using $C–(CO)(Cl)(H_2)$ = −6.2 kcal mol^{-1} from data in ref 10. [e] By additivity[7] and using $C–(Cl)(C_2)(H)$ = −13.7 kcal mol^{-1} from data in ref 10. [f] By additivity[7] and using $C–(Br)(C)(H_2)$ = 4.5 kcal mol^{-1} from data in ref 10. [g] By additivity[7] and using C(Br)(CO)(C)(H) = −0.8 kcal mol^{-1} from data in ref 10. [h] Reference 1. [i] Reference 2. [j] Compare $D(C_2H_5–H)$ = 100.3 kcal mol^{-1}.[11]

$\Delta H_f°(CH_2Br_2) = -1.4$ kcal mol^{-1}, the mean of the latter two. This is also the value quoted in a much earlier collection.[12]

Haloethyl Radicals. The results for these species are given in Table II; again the estimated uncertainty is ±2 kcal mol^{-1}. No $\Delta H_f°$ values have previously been reported for the β-haloethyl radicals. The $\Delta H_f°$ values found in the present work are in keeping with such substitution having no significant effect on $\Delta H_f°$ other than that accompanying halogen substitution in an alkane,[10] i.e., −6 to −7 kcal mol^{-1} for chlorine and +5 to +6 kcal mol^{-1} for bromine. The bond dissociation energies $D(XCH_2CH_2–H)$ are thus not significantly different from $D(CH_3CH_2–H) = 100 \pm 1$ kcal mol^{-1}. The question as to whether these radicals are symmetrical, bridged species or not has been considered from kinetic studies of photobromination[13] and by ESR spectra in solution.[14] The latter conclude that although the chlorine atom is displaced toward the radical center, the radical is not a bridged structure.

Similar results on the tetramethyl-substituted bromoethyl radical have been obtained by Maj et al.,[15] who concluded, inter alia, that migration of Br from carbon to carbon is rapid on the ESR time scale.

For the β-bromoethyl radical, the bond dissociation energy $D(CH_2CH_2–Br)$ is quite small, ca. 7 kcal mol^{-1} [$\Delta H_f°(C_2H_4)$ = 12.5 kcal mol^{-1}; $\Delta H_f°(\dot{B}r)$ = 26.7 kcal mol^{-1} [12]], making the radical difficult to investigate in the gas or condensed phases at ambient temperatures. One method of investigating such relatively unstable species is to neutralize the corresponding cation by electron transfer from a target atom, the reaction being performed on high-velocity, mass-selected ions in a modified mass spectrometer.[16] The charge transfer is a vertical process. The technique, named neutralization-reionization (NR) mass spectrometry, has recently been reviewed.[17,18] In the present work, $[CH_2CH_2{}^{79}Br]^+$ ions, produced by electron impact on $BrCH_2CH_2Br$, were mass selected and neutralized by electron transfer from Xe; the *neutral* products were reionized by collision with O_2 as target gas. The resulting NR mass spectrum contained a significant peak at *m*/*z* 107 showing that the neutral radical has been produced in the neutralization step. Note that the *ion* has a symmetrical bridged structure;[19] the radical, although unsymmetrical, very probably has a low barrier for carbon to carbon migration of the Br atom, and so vertical neutralization of the ion can lead to a stable radical in spite of apparent geometric differences between them.

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Fragmentation of the Enolate Ions of Some Cycloalkanones. A Comparison of High-Energy and Low-Energy Collisional Activation

Swapan Chowdhury and Alex. G. Harrison*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada. *Received March 15, 1988*

Abstract: The collision-induced dissociation reactions of the enolate ions of cyclohexanone, the methylcyclohexanones, and cycloheptanone have been studied following activation by 8-keV collisions and as a function of collision energy over the range 5 to 100 eV (laboratory scale). Those ions which fragment to form detectable products have higher mean internal energies when activated by 50-eV collisions than when activated by 8-keV collisions. This difference is attributed to differences in the mechanism of activation. High-energy collisional activation involves electronic excitation, and those ions which receive large amounts of excitation energy suffer electron detachment before the excess energy can be redistributed as the vibrational energy necessary for bond rupture. On the other hand, low-energy collisional activation involves vibrational excitation of the ion; more energy can be accommodated in vibrational modes before electron detachment occurs. As a result low-energy collisional activation is likely to prove more useful than high-energy collisional activation in the structure elucidation of negative ions of low electron affinity by tandem mass spectrometry.

The analytical uses of negative ion mass spectrometry have undergone considerable development over the past 15 years, particularly in the areas of negative ion chemical ionization[1-3] and negative ion fast atom bombardment.[4,5] These soft ionization techniques usually yield ions characteristic of the molecular weight of the compound of interest but often do not produce the fragment ions which are necessary to derive structural information. Collision-induced dissociation of polyatomic ions has proved[6] to be a powerful method of providing structural information through formation of fragment ions from the "quasi-molecular" ions formed in the initial ionization process. As a consequence there is a continuing interest in the collision-induced fragmentation reactions of gaseous ions, particularly negative ions for which there was relatively little information until recently.[4,5] In addition to the analytical uses, such collisional activation studies provide fundamental information concerning the behavior of gaseous ions.[4,7]

Such collisional activation studies may be carried out by examining ion/neutral collisions in the keV collision energy range using either B/E linked scans in a conventional-geometry mass spectrometer[8] or electric sector scans (the MIKES technique[9]) in a reversed-geometry instrument to detect the product ions. Alternatively, the ion/neutral collisions may occur at low collision energies (5–100 eV) using quadrupole collision cells and quadrupole mass analyzers,[10,11] multi-Fourier transform mass spectrometric (FTMS) techniques,[12,13] or an ion trap mass spectrometer.[14] This low-energy approach has the advantage that the collision energy can be varied readily, the energy-resolved mass spectrometric (ERMS) technique,[10,11,15,16] thus providing qualitative information on the energy dependence of the fragmentation reactions. There is ample evidence, from positive ion studies, that, at these low collision energies, the kinetic energy transformed into internal energy in the ion/neutral collision increases with increasing collision energy,[17-22] although the energy deposited reaches a

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