features observed experimentally could be reproduced by the model, and plots had t_m, maximum intensities, and shapes that corresponded well with the experimental plots. This excellent correlation between the computer model and the data provides support for the kinetics representation summarized in Schemes I and II, but it is possible that other kinetics schemes could fit the data equally well.

The model has been extremely useful in optimizing concentrations and flow rates for obtaining the maximum chemiluminescence signal in analytical applications. For example, we have been able to optimize the conditions in HPLC detection of chemilumophores such as PAH and amino-PAH, as well as dansyl hydrazone derivatives of carbonyl compounds[26] so as to "capture" the signal at its maximum as the reaction products move through the detection cell. This maximum was found to correspond to the sharp burst observed in postphotolysis addition of imidazole. In this way PICL detection limits in flow injection analysis have been improved by a factor of 2 since our earlier paper.[1]

Acknowledgment. We thank Tad Koch, Gary Molander, and Richard Givens for helpful discussions of this work.

Registry No. TCPO, 1165-91-9; IPA, 67-63-0; DPA, 1499-10-1; peroxyoxalate, 119666-18-1; imidazole, 288-32-4.

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(26) Nondek, L.; Milofsky, R. E.; Birks, J. W. *Chromatographia* **1991**, *32*, 33–39.

Heats of Formation of Oxygen-Containing Organic Free Radicals from Appearance Energy Measurements

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Abstract: The appearance energy method for investigating free radical thermochemistry has been shown to produce reliable heats of formation and bond strengths of organic free radicals. The present work centers on the heats of formation at 298 K of hydroxy-substituted alkyl radicals, which, for the most part, are unknown. The present results, in general, agreed well with the limited data available from the literature and are given an uncertainty of ±3 kcal mol^{-1}. It was found that hydroxy substitution in the methyl, ethyl, 1- and 2-propyl, and 2-methylpropyl radicals reduces both primary and secondary C–H bond strengths. The degree of reduction depends on the position of the substituent relative to the bond broken and is greatest for a primary bond with an α-hydroxy group, $\sim$10 kcal mol^{-1}. The result for the hydroperoxy radical, $\Delta H_f°(HO_2{}^\bullet) = 3.5$ kcal mol^{-1}, is in excellent agreement with the literature data, whereas the value obtained for the *tert*-butylperoxy radical, $\Delta H_f°((CH_3)_3COO^\bullet) = -25.2$ kcal mol^{-1}, differs significantly from the literature value. Radical heats of formation were also measured for ${}^\bullet CH_2CH_2OH$ ($\Delta H_f° = -13.5$ kcal mol^{-1}), $CH_3\dot{C}HOH$ ($\Delta H_f° = -14.5$ kcal mol^{-1}), ${}^\bullet CH_2CH_2CH_2OH$ ($\Delta H_f° = -16.0$ kcal mol^{-1}), ${}^\bullet CH_2CH(OH)CH_3$ ($\Delta H_f° = -23.0$ kcal mol^{-1}), ${}^\bullet CH_2C(OH)(CH_3)_2$ ($\Delta H_f° = -35.2$ kcal mol^{-1}), $CH_3\dot{C}HCH_2OH$ ($\Delta H_f° = -18.8$ kcal mol^{-1}), $(CH_3)_2\dot{C}OH$ ($\Delta H_f° = -25.6$ kcal mol^{-1}), $HO\dot{C}HCH_2OH$ ($\Delta H_f° = -52.6$ kcal mol^{-1}), ${}^\bullet CH_2C(O)OH$ ($\Delta H_f° = -61.6$ kcal mol^{-1}), ${}^\bullet CH_2C(O)OCH_3$ ($\Delta H_f° = -57.5$ kcal mol^{-1}), ${}^\bullet CH_2OCH_2CH_3$ ($\Delta H_f° = -10.6$ kcal mol^{-1}), ${}^\bullet C(O)OH$ ($\Delta H_f° = -46.0$ kcal mol^{-1}), ${}^\bullet C(O)OCH_3$ ($\Delta H_f° = -39.9$ kcal mol^{-1}), $HC(O)O^\bullet$ ($\Delta H_f° = -37.7$ kcal mol^{-1}), $CH_3C(O)O^\bullet$ ($\Delta H_f° = -51.7$ kcal mol^{-1}).

Introduction

Recent work from this laboratory[1,2] has clearly demonstrated that the use of electron impact induced dissociative ionization of selected molecules can lead to accurate values for the heat of formation of organic free radicals. The criteria necessary for the success of such experiments have been described in detail.[2] In general, the work to date[1-4] has mostly centered upon free radicals for which results had been obtained by conventional kinetic studies of gas-phase reactions[5] or equilibrium data measured by electron paramagnetic resonance spectroscopy.[6] However, inspection of the last detailed collection[7] of $\Delta H_f°$ values for free radicals and related bond strengths shows a considerable lack of reliable data for oxygen-containing free radicals, and so the present work was undertaken.

Experimental Section

The apparatus used and its operation has been described.[8] Fragment ion–radical pairs were generated in the gas phase by impact of an energy-resolved electron beam from an electrostatic electron monochromator. The appearance energy (AE) of a given ion was determined by detecting the threshold for an ion current at the appropriate mass as the energy of the electron beam was increased in 0.02-eV steps. The energy scale was calibrated against H_2O. The apparatus and sample inlet systems operated at room temperature.

Normal and metastable ion (MI) mass spectra were recorded using a VG ZAB-2F mass spectrometer.[9]

Compounds were of the highest purity commercially obtainable.

Results and Discussion

Table I contains the results obtained for the radicals studied. All $\Delta H_f°$ values used hereafter are for 298 K. Parent molecules with heats of formation obtained from Benson additivity[10] have an estimated uncertainty in their heats of formation of ±1 kcal mol^{-1}. The error for those molecules listed in Pedley et. al.[11] is

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(1) Holmes, J. L.; Lossing, F. P.; Maccoll, A. *J. Am. Chem. Soc.* **1988**, *110*, 7339.

(2) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988**, *110*, 7343.

(3) Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1984**, *58*, 1133.

(4) Holmes, J. L.; Lossing, F. P. Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 1086.

(5) Tschuikow-Roux, E.; Salomon, D. R. *J. Phys. Chem.* **1987**, *91*, 699. Tschuikow-Roux, E.; Salomon, D. R.; Paddison, S. *J. Phys. Chem.* **1987**, *91*, 3037. Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* **1987**, *19*, 15.

(6) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655.

(7) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(8) Lossing, F. P.; Traeger, J. C. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *9*, 19.

(9) Burgers, P. C.; Holmes, J. L.; Szulejko, J. E.; Mommers, A. A.; Terlouw, J. K. *Org. Mass Spectrom.* **1983**, *18*, 254.

(10) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(11) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

0002-7863/91/1513-9723$02.50/0

Table I. Experimentally Determined Appearance Energies, AE, of Counterions, Y^+, from Precursors, RY, and Calculated ΔH_f° (estimated uncertainty ±3 kcal mol^{-1}) of Product Radicals, $R^\bullet$, and Bond Strengths, $D(R-H)$[a]

	$R^\bullet$	Y^+	$\Delta H_f^\circ(RY)^a$	$\Delta H_f^\circ(Y^+)^c$	$AE(Y^+)$	$\Delta H_f^\circ(R^\bullet)$
1	CH_2CH_2OH	CH_3CO	−93.0	156	10.20	−13.8
2		$(CH_3)_3C$	−81.0	166	10.14	−13.2
3		CH_3OCHCH_3	−102.0	132	9.56	−13.5
						av −13.5
	$\Delta H_f^\circ(RH)^{11} = -56.2$				$D(R-H) = 94.8$	
4	CH_3CHOH	CH_3CHOH	−112.0	139	10.26	−14.4
5		CH_2NH_2	−57.1	178	9.56	−14.6
						av −14.5
	$\Delta H_f^\circ(RH)^{11} = -56.2$				$D(R-H) = 93.8$	
6	$CH_2CH_2CH_2OH$	CH_3CO	−97.7	156	10.30	−16.2
7		CH_3CHOH	−111.0	139	10.16	−15.7
						av −16.0
	$\Delta H_f^\circ(RH)^{11} = -61.0$				$D(R-H) = 97.1$	
8	$CH_2CH(OH)CH_3$	CH_3CHOH	−115.5	139	10.02	−23.4
9		$(CH_3)_2COH$	−125.0	119	9.60	−22.6
						av −23.0
	$\Delta H_f^\circ(RH)^{11} = -65.2$				$D(R-H) = 94.3$	
10	$CH_2C(OH)(CH_3)_2$	$(CH_3)_2COH$	−133.0	119	9.40	−35.2
	$\Delta H_f^\circ(RH)^{11} = -74.7$				$D(R-H) = 91.6$	
11	CH_3CHCH_2OH	CH_2OH	−104.0	168	10.98	−18.8
	$\Delta H_f^\circ(RH)^{11} = -61.0$				$D(R-H) = 94.3$	
12	$(CH_3)_2COH$	$(CH_3)_2COH$	−128.0	119	9.60	−25.6
	$\Delta H_f^\circ(RH)^{11} = -65.2$				$D(R-H) = 91.7$	
13	$HOCHCH_2OH$	$(CH_3)_3C$	−120.0	166	10.12	−52.6
	$\Delta H_f^\circ(RH)^{11} = -92.6$				$D(R-H) = 92.1$	
14	$CH_2C(O)OH$	$(CH_3)_3C$	−129.0	166	10.12	−61.6
	$\Delta H_f^\circ(RH)^{11} = -103.4$				$D(R-H) = 93.9$	
15	$CH_2C(O)OCH_3$	$(CH_3)_3C$	−124.0	166	10.04	−58.5
16		CH_3CO	−138.0	156	10.30	−56.5
						av −57.5
	$\Delta H_f^\circ(RH)^{11} = -98.4$				$D(R-H) = 93.0$	
17	$CH_2OCH_2CH_3$	$CH_3CH_2OCH_2$	−99.0	145	10.12	−10.6
	$\Delta H_f^\circ(RH)^{11} = -51.7$				$D(R-H) = 93.2$	
18	$C(O)OH$	CH_3CO	−127.0	156	10.28	−45.9
19		$(CH_3)_2CH$	−115.0	192	11.28	−46.9
20		CH_2Cl	−104.0[11]	227[37]	12.34	−46.4
21		CH_3OCH_2	−134.0	157	10.68	−44.7
						av −46.0
	$\Delta H_f^\circ(RH)^{11} = -90.5$				$D(R-H) = 96.6$	
22	$C(O)OCH_3$	$(CH_3)_2CH$	−110.0	192	11.42	−38.6
23		$(CH_3)_3C$	−118.1[11]	166	10.64	−38.7
24		CH_3CO	−122.0	156	10.24	−41.9
25		CH_3OCH_2	−129.0	157	10.74	−38.3
26		CH_3CHOH	−141.0	139	10.32	−42.0
						av −39.9
	$\Delta H_f^\circ(RH)^{11} = -85.0$				$D(R-H) = 97.2$	
27	HO_2	$(CH_3)_3C$	−58.8[11]	166	9.90	3.5
	$\Delta H_f^\circ(RH)^{18} = -32.6$				$D(R-H) = 88.2$	
28	$(CH_3)_3COO$	$(CH_3)_3C$	−83.4[11]	166	9.72	−25.2
	$\Delta H_f^\circ(RH)^{11} = 58.8$				$D(R-H) = 85.7$	
29	$HC(O)O$	$(CH_3)_3C$	−112.0	166	10.42	−37.7
30		CH_3OCH_2	−125.0	157	10.60	−37.6
						av −37.7
	$\Delta H_f^\circ(RH)^{11} = -90.5$				$D(R-H) = 104.7$	
31	$CH_3C(O)O$	C_2H_5	−106.1[11]	216	11.74	−51.4
32		CH_3OCH_2	−138.0	157	10.54	−51.9
						av −51.7
	$\Delta H_f^\circ(RH)^{11} = -103.4$				$D(R-H) = 103.8$	

[a] All values in kcal mol^{-1} except AE (eV). [b] All values from Benson additivity unless otherwise specified. [c] All values from ref 18 unless othewise stated.

typically better than ±1 kcal mol^{-1}. The reproducibility of threshold energies for calibrant and sample gives an uncertainty in the AE value of ±0.05 eV. The cation heats of formation have an uncertainty of ±1 kcal mol^{-1}. The estimated error of the final ΔH_f° given in the tables is ±3 kcal mol^{-1}. Agreement among the values obtained for the heat of formation of a radical generated from more than one precursor was generally good, with the largest range being 3.7 kcal mol^{-1} for $^\bullet C(O)OCH_3$.

The appearance energy method for determining radical heats of formation requires that the desired ion–radical pair be formed by a process that does not have a significant kinetic shift or reverse energy barrier. Otherwise, the simple relationship

$$\Delta H_f^\circ(\mathrm{R}^\bullet) = \Delta H_f^\circ(\mathrm{RY}) + \mathrm{AE}(\mathrm{Y}^+) - \Delta H_f^\circ(\mathrm{Y}^+) \qquad (1)$$

can only yield an upper limit for the radical heat of formation. A simple bond cleavage in a molecular ion is usually chosen to produce the ion–radical pair because such dissociations predominantly meet these criteria, e.g. (Table I, **1**)

$$\mathrm{CH_3C(O)CH_2CH_2OH^{\bullet+} \rightarrow CH_3\overset{+}{C}O + {}^\bullet CH_2CH_2OH}$$

As the result of a suggestion by a reviewer, a more general problem must be aired. It concerns the temperature applicable to the product ion and radical. This has been considered in detail for photoionization thresholds by Traeger and McLoughlin,[12] following earlier work by Chupka.[13] The basic difficulties are (a) how to identify the meaningful onset energy and (b) how to correct this energy for the contribution toward the activation process from the molecule's initial thermal internal energy. For photoionization experiments this is achieved (a) by linearly extrapolating to zero a *selected* post-threshold portion of the ion yield vs photon energy curve and (b) equating this energy, $\mathrm{AE_{expmt}(Y^+)}$, to $\mathrm{AE_0(Y^+)}$ (the zero Kelvin enthalpy change for the reaction, ΔH°_0) minus that fraction of the internal (thermal) energy, E_i, which is effective in the dissociation. If the desired product enthalpies of formation are for 298 K, then $\mathrm{AE_{298\ expmt}(Y^+)}$ can be derived from an experiment conducted at that temperature. It has been assumed[12,13] that *all* the rotational and vibrational energy of the precursor molecule, RY (at 298 K), is operative in the decomposition of the transition state and so E_i can be evaluated from the usual thermodynamic heat capacity terms. The final equation,[12] in terms of the appearance energy $\mathrm{AE_{298\ expmt}(Y^+)}$, is given by

$$\mathrm{AE_{298\ expmt}(Y^+)} = \Delta H_f{}^\circ{}_{298}(\mathrm{Y^+}) + \Delta H_f{}^\circ{}_{298}(\mathrm{R^\bullet}) - \Delta H_f{}^\circ{}_{298}(\mathrm{RY}) - \left\{\int_0^{298} \mathrm{Cp(Y^+)} + \int_0^{298} \mathrm{Cp(R^\bullet)} - {}^5\!/_2RT\right\} \quad (2)$$

where $\mathrm{Cp(Y^+)}$ and $\mathrm{Cp(R^\bullet)}$ are the molar heat capacities of the products and ${}^5/_2RT$ is the term related to the translational energy deficit of the products.[12]

This approach was clearly justified for a number of small molecules, e.g. NH_3 and H_2O,[12] where the full inclusion of internal energies was required in order to give a satisfactory standard ΔH_f° for the fragment ions, using the selected extrapolated photoionization AE values. The choice of the linear portion of the latter often appears to be straightforward,[12] but in some cases (e.g. the photoionization AE for $C_7H_7^+$ ions from toluene[14]) it may appear somewhat arbitrary.

If the threshold energies chosen in the electron impact experiments have the same significance as those for photodissociation, they should be corrected by adding to them the terms in braces in eq 2, before calculating a $\Delta H_f{}^\circ{}_{298}$ value for a product ion or neutral. Linear extrapolation of our energy selected electron impact AE curves is not possible (see Figure 1). A small part of their curvature at the foot arises from the electron energy distribution (typically ca. 50 meV at half-width), a feature much amplified in the calibrant curve. It should be noted that, unlike the calibrant ionization energy (IE) plot which is linear over a short range, the AE *curves* for the polyatomics contain a large number of unresolved discontinuities arising from a multitude of vibrational states. It is worth emphasizing that, unlike thresholds measured with electrons having the wide energy spread typical of those from a normal ion source filament, the thresholds reported here do not depend significantly on the sensitivity at which the ions are detected, i.e. further data accumulation does not lead to ever lower values for the AE.

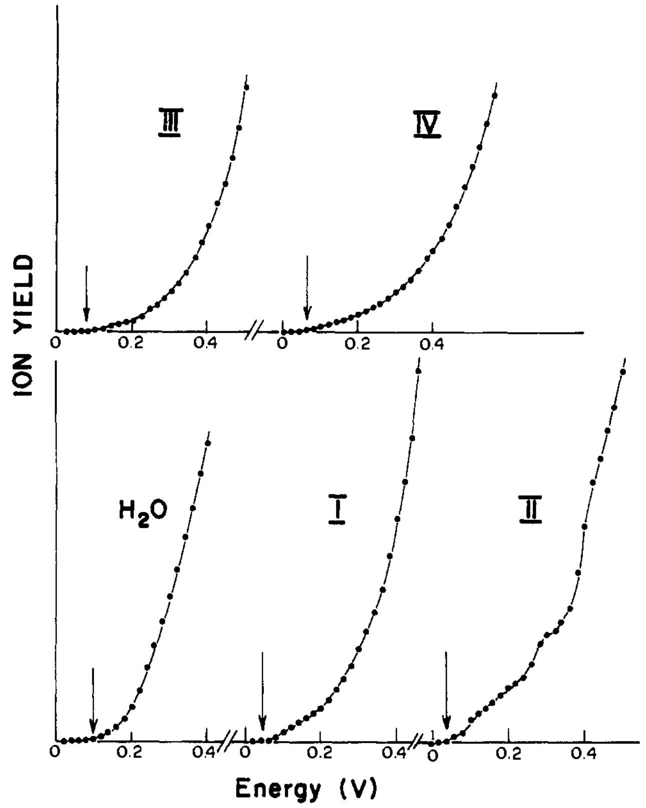

Figure 1. Ion yield vs electron energy for calibration standard (H_2O) and appearance energy curves I → IV for the specific fragment ion from compounds **4**, **2**, **5**, and **3**, respectively (see Table I). The arrows show the selected threshold. Each curve was the average of 100 or more scans.[8]

We are not convinced that the measured electron impact appearance energy represents a threshold lower than the correct value by an energy equal to the sum of the heat capacity terms in eq 2. Indeed for polyatomic ions, we question that all or even a major fraction of the internal thermal energy participates in the activation process. If this were not so, then *without such correction*, the derived $\Delta H_f{}^\circ{}_{298}$ values for many EI experiments reported elsewhere would all be too low by as much as 5 kcal mol^{-1} or more. See, for example, the recent values[1] for $\Delta H_f{}^\circ{}_{298}(\mathrm{C_2H_5^\bullet})$ which are independent of precursor molecule size and very close to the accepted value obtained by a variety of other methods. A further example is the observed threshold energy for the products, ionized but-2-ene and acetaldehyde, from the dissociative ionization of hexanal.[15] For this 19-atom molecule the calculated AE using 298 K ΔH_f° values, 9.87 eV, was very close to the observed value 9.89 eV.

In a recent study of ionization energies,[16] particular attention was paid to the possible "tailing" of the energy selected electron impact IE threshold curves as a result of "hot bands" (i.e. the effect of thermally populated, low-lying excited states of the molecule), but none appeared in those experiments at the highest sensitivity.

The question of kinetic shift for simple bond cleavages which involve metastable molecular ions has also been considered.[17] For the loss of halogen atom from ionized phenyl chloride, bromide, and iodide the residual kinetic shift in the limiting rate constant range appropriate to the present AE measurements, ca. 10^3 s^{-1}, was small indeed, less than 0.2 eV for the worst case, C_6H_5Cl, where the average kinetic energy released in the μs time scale (k

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[12] Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

[13] Chupka, W. A. *J. Chem. Phys.* **1971**, *54*, 1936.

[14] Traeger, J. C.; McLoughlin, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *27*, 319. See also: Buschek, J. M.; Ridal, J. J.; Holmes, J. L. *Org. Mass Spectrom.* **1988**, *23*, 543.

[15] Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860.

[16] Holmes, J. L.; Lossing, F. P. *Org. Mass Spectrom.* **1991**, *26*, 537.

[17] Burgers, P. C.; Holmes, J. L. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 15.

$\simeq 10^5$–10^6 s^{-1}) was also the largest, ca. 0.09 eV. For phenyl iodide the corresponding values were <0.1 and 0.048 eV. Thus the non-inclusion of a kinetic shift term appears justifiable for simple bond cleavages having no reverse energy barrier and, if metastable, only small average kinetic energy releases (say ≤0.05 eV). Only three of the reactions in the present study were metastable processes, and for reactions 9, 12, and 16 the average kinetic energy releases were all less than 0.05 eV.

The inclusion of the remaining correction for translational energy loss (1.5 kcal mol^{-1} at 298 K) should only be made if the other correction factors can be identified and quantified. Our experience to date indicates that for polyatomic systems the effects essentially cancel out. Without clear evidence for the degree of participation of internal (thermal) energies in polyatomic ion fragmentations and its relationship with the measured threshold, we argue that no correction is better than one incorrectly identified and applied. The effects of kinetic shift, internal energy, and the $^5/_2RT$ term operate in opposite directions—the first being added to the appearance energy and the latter two subtracted. Therefore, in this work no numerical value has been given to this unquantified source of possible error.

For the larger precursor molecules used in this study, there is the possibility that there may be alternative reaction pathways which form the appropriate fragment ion, processes which may be thermochemically equivalent to, or even more favorable than, the simple bond cleavage. For this to be so, the desired neutral fragment formed by the simple bond cleavage must be capable of being subdivided into chemically reasonable radicals and molecules. For example, consider a molecular ion, $M^{\bullet+}$, which shows a prominent $[M - C_3H_7O^\bullet]^+$ peak in its normal mass spectrum. Instead of the single loss of an intact $C_3H_7O^\bullet$ radical, the sequential losses of $C_3H_5^\bullet$ and H_2O (or vice versa), CH_4 and $C_2H_3O^\bullet$, $CH_3^\bullet$ and C_2H_4O, etc. could in principle be involved. The normal mass spectrum must therefore be inspected for the necessary intermediate *m/z* values corresponding to any of the above alternative fragmentation routes. The examination of metastable ion mass spectra provides useful additional information, in that they can confirm the parent ion–fragment ion relationships. In order to determine if an alternative pathway is thermochemically competitive, there are two energy terms which must be taken into account. These are (a) the sum of the heats of formation of all *neutral* intermediates and (b) whether the energy barrier for any reaction in an alternative pathway exceeds the observed threshold for the desired reaction. It is convenient at this point to define a value, δ, which is the difference, $\sum[\Delta H_f°$(neutral intermediates)] – $\Delta H_f°$(radical fragment). If the sum of the enthalpies of the proposed neutral intermediates exceeds the $\Delta H_f°$ (radical fragment) obtained from the measured AE, then δ is positive and the alternative channel cannot compete. If δ is zero or negative, then the alternative pathway could in principle compete with the simple bond cleavage. It is then necessary to determine if the energy barrier for the alternative pathway exceeds the observed threshold (case (b) above). An example is the production of the 3-hydroxypropyl radical, $^\bullet CH_2CH_2CH_2OH$, from ionized 5-hydroxypentan-2-one (**6**, Table I). Loss of H_2O and $C_3H_5^\bullet$ yields a δ value of –2.9 kcal mol^{-1}. It was necessary, therefore, to measure the appearance energy of the intermediate ion, $[C_5H_{10}O_2 - H_2O]^{\bullet+}$, *m/z* 84. The result showed that the minimum energy barrier for the alternative pathway was greater than that for the desired reaction by at least 0.4 eV.

Table II contains the alternative pathways for the formation of the desired counterion which are the closest thermochemical competitors with the simple bond cleavage. For example, in 1–3, the energy requirement for the production of neutral fragments $H\dot{C}O$ and CH_4 is lower than that for any other neutral pair of total elemental composition $C_2H_5O^\bullet$ ($\sum\Delta H_f°$ values[18] (kcal mol^{-1}) are $H\dot{C}O + CH_4 = -7.1$, $H_2 + {}^\bullet CH_2OH = -6.2$, $C_2H_3^\bullet + H_2O = 5.6$, $CH_3^\bullet + CH_2O = 8.8$, $H^\bullet + CH_3CHO = 12.5$, $C_2H_4 + {}^\bullet OH = 21.8$, $C_2H_5^\bullet + O = 87.6$). Reactions corresponding to simple bond cleavages and which are also metastable processes are found to provide reliable heats of formation of the radicals in question. The compound 1,4-pentanediol (**7**), another 3-hydroxypropyl radical precursor, also exhibits the reverse reaction, losing $C_3H_5^\bullet$ first. Again, the AE of the intermediate ion $[C_5H_{12}O_2 - C_3H_5^\bullet]^+$, *m/z* 63, was found to be greater than that of the desired fragment ion at *m/z* 45. The isomeric radical, $CH_3\dot{C}HCH_2OH$, is produced from 2-methyl-1,3-propanediol (**11**), whose molecular ion was observed in its MI mass spectrum to lose $CH_3\dot{C}O$ followed by CH_4 resulting in a δ of –4.0. An appearance energy of the intermediate ion at *m/z* 47, $[C_2H_7O]^+$, showed that this process could not compete with the desired simple bond cleavage. The only exception was item 13 in Table I, for which the energy barrier to consecutive losses of H_2O and CH_3CO was found to be 0.54 eV less than that of the bond cleavage forming $HO\dot{C}HCH_2OH$, leaving some doubt as to the reliability of the new value.

Table II. Lowest Energy Alternative Processes Producing Counterions, Y^+

reaction	neutral, N_1	$\Delta H_f°$-$(N_1)^{a,18}$	neutral, $N_2{}^b$	$\Delta H_f°$-$(N_2)^{a,18}$	δ^a
1, 2, 3	HCO	10.7	$CH_4{}^c$	–17.8	+6.4
4, 5	HCO	10.7	CH_4	–17.8	+7.4
6, 7	H_2O^d	–57.8	$C_3H_5{}^c$	39.0	–2.8^e
	$C_3H_5{}^d$	39.0	H_2O^c	–57.8	–2.8^e
	CH_3CO^d	–6.0	CH_4	–17.8	–7.8^f
8, 9^g	$C_3H_5{}^d$	39.0	H_2O^c	–57.8	+3.5
	H_2O^d	–57.8	$C_3H_5{}^c$	39.0	+3.5
	CH_3CO^d	–6.0	CH_4	–17.8	–1.6^f
10	$C_4H_7{}^d$	29.0	H_2O^c	–57.8	+4.8
11	CH_3CO^d	–6.0	$CH_4{}^c$	–17.8	–4.0^e
12^g	CH_3CO	–6.0	CH_4	–17.8	+1.8^h
13	H_2O^d	–57.8	CH_3CO^c	–6.0	–10.2
14	CO_2	–94.1	$CH_3{}^c$	34.8	+2.3
15, 16^g	CH_3CO	–6.0	CH_2O^c	–26.0	+25.5
	$C_3H_3O^d$	17.0	H_2O	–57.8	+16.7^f
17	$CH_3{}^d$	34.8	CH_3CHO^c	–39.6	+6.0
	CH_3CO^d	–6.0	CH_4	–17.8	–13.0^f
	H_2O^d	–57.8	C_3H_5	39.0	–8.0^f
18–21	H	52.1	CO_2	–94.1	+3.8
22–26	CH_3	34.8	CO_2	–94.1	–19.4^i
	CO_2	–94.1	CH_3	34.8	–19.4^i
27	H	52.1	O_2	0.0	+48.6
28	$(CH_3)_3C$	11.0	O_2	0.0	+36.2
29, 30	H	52.1	CO_2	–94.1	–4.1^j
	CO_2	–94.1	H	52.1	–4.1^j
31, 32	CH_3	34.8	CO_2	–94.1	–7.8^k
	CO_2	–94.1	CH_3	34.8	–7.8^k

[a] kcal mol^{-1}. [b] All intermediate ions were observed in the normal mass spectrum, unless otherwise stated. [c] Neutral loss observed in the MI mass spectrum of intermediate ion. [d] Neutral loss observed in the MI mass spectrum of parent ion. [e] AE(intermediate ion) < AE(Y^+) by at least 9 kcal mol^{-1}. [f] Intermediate ion does not yield Y^+. [g] Counterion Y^+ observed in the MI mass spectrum of parent ion. [h] Neither neutral loss was observed to be a metastable process. [i] Neither possible intermediate ion was observed in the normal mass spectra of 23–26; only $[M - CH_3]^+$ was observed in the normal mass spectrum of 22 (see text). [j] Neither possible intermediate ion was observed in the normal mass spectrum of 29; for discussion of 30, see text. [k] Neither possible intermediate ion was observed in the normal mass spectrum of 31; only $[M - CH_3]^+$ observed in normal mass spectrum of 32 (see text).

For **22–26**, which form the $^\bullet C(O)OCH_3$ radical, none of the normal mass spectra of the parent molecules contains a peak due to loss of carbon dioxide and only one, **22**, contains a peak due to methyl loss. However, the ion formed by methyl loss from methyl isobutyrate, *m/z* 87, is not metastable with respect to loss of CO_2. In the case of $HC(O)O^\bullet$, the ester HC(O)O-*t*-Bu (**29**) has neither $[M - H]^+$ nor $[M - CO_2]^{\bullet+}$ in its normal mass spectrum. This precludes the stated alternative pathway (see Table II). Only a weak loss of 44 u. was observed in the MI mass spectrum of the $[M - H]^+$ ion from methoxymethyl formate (**30**). The initial barrier to $H^\bullet$ loss should be sufficient to preclude this pathway from competition with the desired bond cleavage. Ethyl

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(18) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. In *J. Phys. Chem. Ref. Data Supp. 1* **1988**, *17*.

acetate (**31**) has neither $[M - CH_3]^+$ nor $[M - CO_2]^{\bullet+}$ in its normal mass spectrum, eliminating their competition with the desired bond cleavage. The normal mass spectrum of methoxymethyl acetate (**32**) has a peak at $[M - 15]^+$ but not at $[M - 44]^{\bullet+}$. Methyl loss from the molecular ion was not observed to be a metastable process, thus eliminating this alternative pathway from competition with the simple bond cleavage.

Before discussing the results in detail, some remarks must be made concerning the heats of formation of the neutral diols used in this study (Table I, **4**, **7–13**). A significant problem arises with the 1,3-diols. In this work we used ΔH_f° values calculated by additivity rather than those available from, or based on, experimental values found in the most recent compilation.[11] Of the nine alkane diols in ref 11, except for 1,3-propanediol, 1,3-butanediol, and 2,3-butanediol, the ΔH_f° values agree with additivity based values to within 1 kcal mol^{-1}. For the first two diols above, the reference values are 3 kcal mol^{-1} more *positive* than those calculated by additivity. It is difficult to see how such discrepancies can arise, there being no obvious anomaly, such as a suspect ΔH°_{vap} value,[11] and no likely physicochemical explanation (e.g. based on molecular geometry or H-bonding effects) comes to mind. Gardner and Hussain,[19] in the original calorimetric work, noted that ΔH_f° of 1,3-propanediol appeared to be too high by ~4 kcal mol^{-1}. However, like us, they could find no obvious explanation. Thus, for the diols **8–11** in Table I, the $\Delta H_f^\circ(RY)$ values could be estimated by modifying the experimentally derived values[11] for 1,3-propanediol, using appropriate additivity terms for methyl substitution. This would give ΔH_f° values greater by +3 kcal mol^{-1} than those from additivity alone. If the additivity based values are incorrect then this may manifest itself in anomalously low C–H bond strengths for **8–11** (see later discussion).

For 2,3-butanediol (**4**), the experimental ΔH_f° is 4.7 kcal mol^{-1} more *negative* than the additivity based value. The experimental ΔH°_{vap}[11] appears to be too low when compared with all of the other diols, having a Trouton's constant of 31 eu (cal mol^{-1} K^{-1}) compared with 34.5 eu for $(CH_2OH)_2$ and 33.3 eu for $CH_3CH(OH)CH_2OH$, but this does not suffice to explain the 4.7 kcal mol^{-1} difference. A value of −112.0 kcal mol^{-1} was selected, slightly more negative than the additivity result, −111.0 kcal mol^{-1}. As will be seen, this does not produce an anomaly in the thermochemical data discussed below.

It is now appropriate to compare the present data with values from the literature and to discuss the significance of new values.

A previous attempt[20] at estimating the heat of formation of the 2-hydroxyethyl radical assumed a bond strength, $D(R-H)$, equal to that in ethane (100.7 kcal mol^{-1} [21]) yielding a value for $\Delta H_f^\circ(HOCH_2CH_2^\bullet)$ of −7.5 kcal mol^{-1}. McMillen and Golden[7] list a value of 94 ± 2 kcal mol^{-1} for the bond strength which is in excellent agreement with the present value of 94.8 kcal mol^{-1}. For $CH_3\dot{C}HOH$, a previous determination from this laboratory[3] of the heat of formation gave −17.7 kcal mol^{-1}, in poor agreement with the value listed by McMillen and Golden,[7] −15.2 kcal mol^{-1}. We have modified the heat of formation of the precursor molecule $CH_3CH(OH)CH(OH)CH_3$ (**4**) (see above discussion on diol thermochemistry) resulting in a $\Delta H_f^\circ(CH_3\dot{C}HOH)$ of −14.4 kcal mol^{-1}, in close agreement with the value obtained from $CH_3CH(OH)CH_2NH_2$, −14.6 kcal mol^{-1}. Both values are now in good agreement with that in ref 7. Two separate experimental determinations of $\Delta H_f^\circ((CH_3)_2\dot{C}OH)$ by Benson,[22,23] using the iodine abstraction method, gave −27 kcal mol^{-1} for the heat of formation and 90.5 kcal mol^{-1} for $D(H-C(OH)(CH_3)_2)$, in good agreement with our values of −25.6 and 91.7 kcal mol^{-1}. The heat of formation of the 2-hydroxypropyl radical, $^\bullet CH_2CH(OH)CH_3$, was estimated from group additivity[24] to be −18.8 kcal mol^{-1}, 4.2 kcal mol^{-1} higher than our value of −23.0 kcal mol^{-1}.

The heat of formation of the resonance stabilized carboxymethyl radical (**14**) has been estimated from semiempirical calculation[25] to be −59.1 kcal mol^{-1} and from trends in experimentally determined $^\bullet CH_2OR$ heats of formation[26] to be −58.1 kcal mol^{-1}, both in reasonable agreement with our result of −61.6 kcal mol^{-1}.

From RRKM theory[27] a heat of formation for $^\bullet C(O)OH$ of −50.7 kcal mol^{-1} and $D(H-C(O)OH)$ = 91.9 kcal mol^{-1} have been estimated. More recently a value of −53.2 ± 0.6 kcal mol^{-1} was derived from a photoionization mass spectrometry study.[28] This result was based upon a new determination of $\Delta H_f^\circ(C(O)OH)^+$ = 143 kcal mol^{-1} and the ionization energy of the radical generated by the reaction of $F^\bullet$ with formic acid. This leads to a lower strength for the above bond, 90.1 kcal mol^{-1}. Our result of ΔH_f° = −46.0 kcal mol^{-1} gives a considerably higher value for the bond strength, 96.6 kcal mol^{-1}. Ab initio calculations, at the 6-311G**//MP3 level, by Tse[29] on the reaction of $HO^\bullet + CO$ yield a significantly higher value for the heat of formation of $^\bullet C(O)OH$, −36.5 kcal mol^{-1}, with a barrier to fragmentation to $HO^\bullet + CO$ of 2.8 kcal. Calculations by Schatz et al.[30] gave −41.6 kcal mol^{-1}, but they modified this value to −51.1 kcal mol^{-1} following consideration of experimental data from the literature. Thus there is poor agreement between the above values for $\Delta H_f^\circ(^\bullet C(O)OH)$. The difference between the present results and the ΔH_f° of Ruscic et al.,[28] 6.5 kcal mol^{-1}, is difficult to rationalize, particularly since our value is based on four independent measurements which lie within a narrow range, −46.0 ± 1.1 kcal mol^{-1}. Our results do agree with a recent value by Schwarz and Dodson,[31] −47.0 kcal mol^{-1}, estimated from the reduction potential of $CO_2^{\bullet-}$ in aqueous solution. Note that we find for the closely related radical $^\bullet C(O)OCH_3$, ΔH_f° = −39.9 kcal mol^{-1}, a bond strength, $D(H-C(O)OCH_3)$ = 97.2 kcal mol^{-1}, similar to that for formic acid.

McMillen and Golden[7] list $\Delta H_f^\circ(^\bullet C(O)OCH_3)$ = −40.4 and 92.7 kcal mol^{-1} for $D(H-C(O)OCH_3)$. However, these values are not mutually compatible; the quoted radical heat of formation, −40.4 kcal mol^{-1}, combined with the reliable heat of formation of $HC(O)OCH_3$, −85.0 kcal mol^{-1}, gives a bond strength of 96.7 kcal mol^{-1}. It would appear that the −40.4 kcal mol^{-1} value is a misprint.

The heat of formation of $HC(O)O^\bullet$ was determined by Nishimura et al.[32] to be −40 ± 6 kcal mol^{-1} from the appearance energy of CH_3^+ from methyl formate, 13.27 ± 0.24 eV. It is in rough agreement with the present result of −37.7 kcal mol^{-1}, but the AE value will certainly be inaccurate; the reaction leading to CH_3^+ is the sixth fragmentation in ascending energy for methyl formate and so kinetic and competitive shifts will be significant. Semiempirical calculations[33] estimate $\Delta H_f^\circ(HC(O)O^\bullet)$ = −35.1 kcal mol^{-1}. The calculations by Schatz[30] give a value of −31.1 kcal mol^{-1}, modified to be −42.2 kcal mol^{-1}, again by reference to experimental data.

The present results for the heat of formation of the $CH_3C(O)O^\bullet$ radical, −51.7 kcal mol^{-1}, and $D(H-O(O)CCH_3)$, 103.8 kcal mol^{-1}, are in reasonable agreement with those in ref 7, −49.6 and 105.8 kcal mol^{-1}. Semiempirical calculations[33] estimate the heat of formation to be −44.0 kcal mol^{-1}.

McMillen and Golden[7] list a value for the heat of formation of $HO_2^\bullet$ of 2.5 kcal mol^{-1}, corresponding to 87.2 kcal mol^{-1} for $D(H-OOH)$. Fisher and Armentrout[34] have recently reported

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(19) Gardner, P. J.; Hussain, K. S. *J. Chem. Thermodyn.* **1972**, *4*, 819.

(20) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 7007.

(21) Castelhano, A. T.; Marriot, P. R.; Griller, D. *J. Am. Chem. Soc.* **1981**, *103*, 4262.

(22) Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125.

(23) Walsh, R.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88* (15), 3480.

(24) Miyoshi, A.; Matsui, H.; Washida, N. *J. Phys. Chem.* **1990**, *94*, 3016.

(25) Khudyakov, I. M.; Burmistrov, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, *1*, 214.

(26) Orlov, V. M.; Misharev, A. D.; Takhistov, V. V.; Ryabinkin, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, *7*, 1514.

(27) Mozurkewich, M.; Lamb, J. J.; Benson, S. W. *J. Phys. Chem.* **1984**, *88*, 6435.

(28) Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1989**, *91* (11), 6780. Ruscic, B.; Schwarz, M.; Berkowitz, J. *J. Chem. Phys.* **1989**, *91* (11), 6772.

(29) Tse, J. S. Private communication.

(30) Schatz, G. C.; Fitzcharles, M. S.; Harding, L. B. *Faraday Discuss. Chem. Soc.* **1987**, *84*, 359.

(31) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(32) Nishimura, T.; Zha, Q.; Meisels, G. G. *J. Chem. Phys.* **1987**, *87* (8), 4589.

(33) Bischof, P.; Friedrich, G. *J. Comput. Chem.* **1982**, *3* (4), 486.

(34) Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 4396.

Table III. A Comparison of Bond Strengths of Hydroxy-Substituted (position X with respect to the bond in question) Alkyl Radicals, R$^{\bullet}$, with Those from the Corresponding Alkyl Radical, A$^{\bullet}$ [a]

A$^{\bullet}$	$\Delta H_f°(\mathrm{A}^{\bullet})$ [b]	$\Delta H_f°(\mathrm{AH})$ [11]	$D(\mathrm{A-H})$ [c]	R$^{\bullet}$	X	$\Delta H_f°(\mathrm{R}^{\bullet})$ [d]	$\Delta H_f°(\mathrm{RH})$ [11]	$D(\mathrm{R-H})$	Δ
CH_3	34.8[38]	−17.8	104.7	$HOCH_2$	α	−5.7[3]	−48.2	94.6	−10.1 (a)
CH_3CH_2	27.8	−20.1	100.0	$HOCH_2CH_2$	β	−13.5	−56.2	94.8	−5.2 (b)
$CH_3CH_2CH_2$	22.7	−25.0	99.8	$CH_3CH(OH)CH_2$	β	−23.0	−65.2	94.3	−5.5 (c)
				$HOCH_2CH_2CH_2$	γ	−16.0	−61.0	97.1	−2.7 (d)
$(CH_3)_2CH$	19.1	−25.0	96.2	CH_3CHCH_2OH	β	−18.8	−61.9	94.3	−1.9 (e)
$(CH_3)_2CHCH_2$	15.8	−32.1	100.0	$(CH_3)_2C(OH)CH_2$	β	−35.2	−74.7	91.6	−8.4 (f)

[a] All values in kcal mol^{-1}. [b] From ref 1 unless otherwise specified. [c] Uses $\Delta H_f°(\mathrm{H}^{\bullet})$ = 52.1 kcal mol^{-1}. [d] This work unless otherwise specified.

$\Delta H_f°(\mathrm{HO_2}^{\bullet})$ to be 3.8 ± 1.2 kcal mol^{-1} and D(H–OOH) to be 88.4 kcal mol^{-1}, from guided ion beam mass spectrometric studies of the reaction of O_2^+ with CH_4. Our values of 3.5 and 88.2 kcal mol^{-1} are in excellent agreement with this result, as well as with that suggested by Shum and Benson,[35] 3.5 kcal mol^{-1}, in a critical analysis of available data. For the *tert*-butylperoxy radical $(CH_3)_3COO^{\bullet}$, Heneghan and Benson[36] reported a heat of formation of −20.7 kcal mol^{-1} and $D(\mathrm{H-OOC(CH_3)_3})$ of 89.4 kcal mol^{-1} from a direct measurement of the equilibrium constant for $\mathrm{Br}^{\bullet} + t\text{-}C_4H_9O_2H \rightleftharpoons t\text{-}C_4H_9O_2^{\bullet} + \mathrm{HBr}$ and an estimate for $\Delta S°$. Our results are lower, −25.2 and 85.7 kcal mol^{-1}. Recalling that the AE method, due to kinetic shift and reverse activation energy, gives at worst *upper* limits for the radical heats of formation, the value obtained by Heneghan and Benson may be too high, possibly arising from uncertainty in $\Delta H_f°(t\text{-BuOOH})$. There are remarkably few[11] values for $\Delta H_f°$(ROOH), making it impossible to check for consistency among them.

Table III contains a comparison of the bond strengths found for the alcohols, D(R–H), with those of the corresponding alkane, D(A–H). The differences between the bond strengths are given by $\Delta = D(\mathrm{R-H}) - D(\mathrm{A-H})$. Most of the heats of formation of the alkyl radicals (A$^{\bullet}$) used in the comparison were those determined in our earlier work,[1] values which compared extremely well with those reported by Griller and Castelhano,[6] all values agreeing within the estimated experimental errors. The trend in the bond strengths in going from primary (~100 kcal mol^{-1}, except for methane) to secondary (96–7 kcal mol^{-1}) to tertiary (~94 kcal mol^{-1}) is evident from both works. For (a), where the OH group replaces hydrogen α to a primary C–H bond, the C–H bond strength is lowered by 10.1 kcal mol^{-1}. The difference (Δ), for a given C–H bond type, is approximately halved for each carbon atom farther away from the bond that the substituent is placed. Thus, β-substitution decreases the strength of a primary bond by ~5 kcal mol^{-1} (b, c), while γ-substitution decreases the bond strength by only ~2.7 kcal mol^{-1} (d). The bond strength in $\mathrm{H-CH_2C(OH)(CH_3)_2}$ is quite low at 91.6 kcal mol^{-1}, indicating a reduction of 8.4 kcal mol^{-1} (f). There is no clear reason why it should be different from the other two β-OH substituted analogues (b, c). The effect on a secondary C–H bond strength is about half that on a primary bond, as β-hydroxy substitution only weakens the bond by 1.9 kcal mol^{-1}, as opposed to 5 kcal mol^{-1} for primary bonds.

If the experimental values[11] for the heats of formation of 1,3-propanediol and 1,3-butanediol are accurate, then it is necessary to add +3 kcal mol^{-1} to the values obtained using additivity terms. If this applies to the similar molecules in Table I, it is necessary to add +3 kcal mol^{-1} to the heats of formation of **8–10**. The resulting radical heats of formation, $\Delta H_f°(^{\bullet}\mathrm{CH_2CH(OH)CH_3})$ = −20.0 kcal mol^{-1}, $\Delta H_f°(^{\bullet}\mathrm{CH_2C(OH)(CH_3)_2})$ = −32.2 kcal mol^{-1}, and $\Delta H_f°(\mathrm{CH_3\dot{C}HCH_2OH})$ = −15.8 kcal mol^{-1}, give bond strengths of 97.3, 94.6, and 97.3 kcal mol^{-1}, respectively. The first two values indicate a lowering of the primary C–H bond strength due to β-OH substitution by 2.5 and 5.2 kcal mol^{-1}, respectively. The former of these values is even less than the observed effect of γ-substitution, 2.7 kcal mol^{-1}! Also, $D(\mathrm{H-CH(CH_3)CH_2OH})$ = 97.3 kcal mol^{-1} means the secondary C–H bond strength has been *increased* by 1.1 kcal mol^{-1} over the simple alkane C–H bond strength. We would argue that these anomalous results justify our choice of the neutral $\Delta H_f°$ values from additivity.

There is also a trend in the heats of formation and bond strengths for consecutive methyl substitution on the $^{\bullet}CH_2OH$ radical. The heats of formation of $^{\bullet}CH_2OH$, −5.7 kcal mol^{-1}, $\mathrm{CH_3\dot{C}HOH}$, −14.5 kcal mol^{-1}, and $\mathrm{(CH_3)_2\dot{C}OH}$, −25.6 kcal mol^{-1}, are separated by ~10 kcal mol^{-1}. From a study of anion reduction potentials in solution, Schwarz and Dodson[31] derived $\Delta H_f°$ values for all three of these radicals, each about 3 kcal mol^{-1} lower than the present results, leading to higher bond strengths. The bond strengths, D(R–H), which follow from our values are 94.6, 93.8, and 91.7 kcal mol^{-1}, respectively. The decrease in bond strength in going from a primary to a tertiary C–H bond in these alcohols parallels the trend in alkanes, but to a lesser degree.

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Registry No. **1**$^{\bullet+}$, 136707-52-3; **2**$^{\bullet+}$, 136707-53-4; **3**$^{\bullet+}$, 136779-41-4; **4**$^{\bullet+}$, 136779-42-5; **5**$^{\bullet+}$, 136779-43-6; **6**$^{\bullet+}$, 136707-54-5; **7**$^{\bullet+}$, 136779-44-7; **8**$^{\bullet+}$, 136779-45-8; **9**$^{\bullet+}$, 136779-46-9; **10**$^{\bullet+}$, 136707-55-6; **11**$^{\bullet+}$, 136707-56-7; **12**$^{\bullet+}$, 136707-57-8; **13**$^{\bullet+}$, 136779-47-0; **14**$^{\bullet+}$, 136707-58-9; **15**$^{\bullet+}$, 136707-59-0; **16**$^{\bullet+}$, 136062-69-6; **17**$^{\bullet+}$, 136707-60-3; **18**$^{\bullet+}$, 97588-96-0; **19**$^{\bullet+}$, 73889-88-0; **20**$^{\bullet+}$, 118574-30-4; **21**$^{\bullet+}$, 136707-61-4; **22**$^{\bullet+}$, 67505-84-4; **23**$^{\bullet+}$, 122872-35-9; **24**$^{\bullet+}$, 136707-62-5; **25**$^{\bullet+}$, 136707-63-6; **26**$^{\bullet+}$, 136779-48-1; **27**$^{\bullet+}$, 117229-38-6; **28**$^{\bullet+}$, 86476-52-0; **29**$^{\bullet+}$, 98603-02-2; **30**$^{\bullet+}$, 110661-94-4; **31**$^{\bullet+}$, 73889-89-1; **32**$^{\bullet+}$, 136707-64-7; $^{\bullet}CH_2CH_2OH$, 4422-54-2; $CH_3{}^{\bullet}CHOH$, 2348-46-1; $^{\bullet}CH_2CH_2CH_2OH$, 6154-13-8; $^{\bullet}CH_2CH(OH)CH_3$, 7277-18-1; $^{\bullet}CH_2C(OH)(CH_3)_2$, 5723-74-0; $CH_3{}^{\bullet}CHCH_2OH$, 7055-10-9; $(CH_3)_2{}^{\bullet}COH$, 5131-95-3; $HO^{\bullet}CHCH_2OH$, 3250-66-6; $^{\bullet}CH_2C(O)OH$, 2887-46-9; $^{\bullet}CH_2C(O)OCH_3$, 54668-31-4; $^{\bullet}CH_2OCH_2CH_3$, 136707-65-8; $^{\bullet}C(O)OH$, 2564-86-5; $^{\bullet}C(O)OCH_3$, 16481-04-2; $HO_2^{\bullet}$, 3170-83-0; $(CH_3)_3COO^{\bullet}$, 3395-62-8; $HC(O)O^{\bullet}$, 16499-21-1; $CH_3C(O)O^{\bullet}$, 13799-69-4.

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(35) Shum, L. G. S.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 3479.

(36) Heneghan, S. P.; Benson, S. W. *Int. J. Chem. Kinet.* **1983**, *15*, 815.

(37) Holmes, J. L.; Lossing, F. P.; McFarlane, R. A. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *86*, 209.

(38) Henegan, S. P.; Knoot, P. A.; Benson, S. W. *Int. J. Chem. Kinet.* **1981**, *13*, 677.