present results raise questions about the existing explanations and models for the NADH/NAD$^+$ couple's action. On the question of NADH's role as a hydride donor vs the e$^-$, H$^+$, e$^-$ transfer sequence, at least in the two photoredox processes of RNAH examined, laser-photolysis studies tend to support the latter mechanism.

Thus in addition to providing a better understanding to the important chemistry exhibited by NADH/NAD$^+$, these compounds have several unique features that allow practical applications in many areas. One can cite, for example, their use as neutral donors for various forms of organized assemblies and biphasic systems and as agents to regenerate NADH in an inexpensive way. In applications of photochemical solar-energy conversion, due to the retention of their chemical identity in the oxidized form, these RNAH molecules can certainly serve as more useful donors than the commonly used "irreversible" donors such as EDTA and tertiary amines.

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Solvent Effects on the Thermochemistry of Free-Radical Reactions[1]

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Abstract: Heats of the reaction $H_2O_2 + 2RH \rightarrow 2H_2O + 2R^\bullet$ were measured in water for a variety of organic substrates by using photoacoustic calorimetry. The values obtained were substantially lower than those calculated from gas-phase data and the difference was due entirely to the change in solvation energy associated with the conversion of 1 equiv of hydrogen peroxide to 2 of water. The solvation energies of $R^\bullet$ and RH were the same and their contributions to the measured heats of reaction therefore cancelled. The results suggest that solution data, measured in extremely polar solvents, can be converted to their gas-phase equivalents (and vice versa) by considering only the heats of solvation of very small, polar molecules that participate in a given reaction. Moderately large organic molecules and their corresponding radicals are solvated to the same extent—even in water.

A knowledge of the thermochemistry for free-radical reactions is of vital importance from practical, mechanistic, and theoretical perspectives.[3] Much of the thermochemical data that is now available to us comes from gas-phase measurements.[4,5] However, a very large proportion of free-radical reactions are carried out in the liquid phase and there has been a nagging doubt as to whether gas-phase data were applicable in this situation because of solvation effects.

The concerns have, to some extent, been mitigated by measurements of homolytic bond dissociation energies in solutions[6] that have generally been in good agreement with gas-phase data.[7] Indeed, in some instances[6] solution data have paved the way for revisions and improvements to gas-phase results. However, essentially all of these measurements have been made in nonpolar solvents where differences in the solvation of reaction products versus starting materials might be expected to be small.

Recently, Katritzky[8] proposed that differential solvation of reactants versus products might indeed be important in polar solvents when the radicals formed in a reaction had larger dipole moments than their precursors. The hypothesis was based on a theoretical treatment and was immediately countered by experimental work.[9] However, in the light of this continuing uncertainty, we decided to tackle the problem of solvation effects by going to an extreme case and by measuring heats of free-radical reactions and bond strengths in a very polar solvent—water.

Experimental Section

Hydrogen peroxide was used extensively in these experiments and a major consideration in the selection of materials and equipment was therefore to ensure that metal ion contamination was minimized.[10]

Materials. Water was distilled and deionized by using a Milli Q water system (Millipore) or was commercially available in a glass-distilled grade (BDH Omnisolv). The hydrogen peroxide used in this work was a 30% solution in water that was subsequently diluted to the requisite concentration. *o*-Hydroxybenzophenone and 2,4-dihydroxybenzophenone were purified by multiple recrystallizations from ethanol or ethanol–water mixtures. All other materials were commercially available in high purity and were used as received.

Apparatus. The photoacoustic calorimeter used in this work has been described in detail elsewhere.[11] Briefly, pulses from a nitrogen laser (Molectron UV24, 337.1 nm, pulse width 10 ns, output 10 mJ/pulse, repetition rate 5 Hz) were used to photolyze solutions contained in a standard quartz flow cell (Hellma 171 QS). The laser light was attenuated by using an iris so that only a fine beam passed through the sample cell. Variations in laser power were monitored by splitting out a small fraction of the attenuated light to a reference detector.

Each pulse initiated free-radical reactions within the sample cell along the trajectory of the photolyzing beam, and the heat evolved in these

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processes caused a shock wave in the solution that was transmitted at the speed of sound to the cell wall where it caused a vibration. These vibrations were detected by using a piezoelectric transducer (Panametrics V101, 5-MHz or 0.5-MHz response) that was clamped to the cell wall. A small quantity of silicon grease was applied to the detecting surface of the transducer so as to improve coupling with the cell. Signals from the transducer were amplified (Panametrics 5670 preamplifier) and were stored and averaged in an oscilloscope (Tektronix 7603).

The transducer detected the initial shock wave and its many reflections, which persisted into the millisecond time scale. However, the time scale of the relevant chemistry that was investigated in this work (vide infra) was such that only the amplitude of the initial wave was of interest. This was shown to be proportional to the amount of heat liberated by changing the concentration of the photolabile substrate and by showing that the amplitude of the wave was directly proportional to the absorption of laser light. Signals from at least 128 laser pulses were averaged to obtain a data point.

In a typical experiment, an aqueous solution containing a substrate (30% v/v) and hydrogen peroxide (0.3–1.75 M) was prepared and was placed in a Pyrex reservoir where it was deoxygenated by nitrogen purging. The solution was flowed slowly (4.5 mL/min) to a quartz UV flow cell situated in a UV–visible spectrophotometer, where its optical absorption was measured, and finally to the sample chamber of the photoacoustic calorimeter. At all times, care was taken to ensure that the solutions did not come into contact with metal surfaces, and Teflon tubing and valves were therefore used to link the various elements of the flow system.

The apparatus was then thoroughly cleaned and was calibrated by using solutions of 2-hydroxybenzophenone or 2,4-dihydroxybenzophenone, which convert all of the absorbed light energy into heat within a few nanoseconds. Since the transmission of the photoacoustic signal is sensitive to the compressibility of the solvent, the same substrate–water mixture was used for the standard as was used in the reaction mixture with the obvious exception that hydrogen peroxide was excluded from the former. Some difficulties were experienced with the use of 2,4-dihydroxybenzophenone as a standard since its absorption spectrum was found to be pH dependent and changed as dissolved carbon dioxide was purged from the solutions. Nitrogen purging was therefore continued until constant values of optical density were obtained.

Results and Discussion

In this work, laser photolysis of hydrogen peroxide in the photoacoustic calorimeter was used as a source of hydroxyl radicals. These, in turn, were used to abstract hydrogen from suitable donors, RH, giving rise to radicals, R$^\bullet$ (eq 1–3). For accurate

$$H_2O_2 \rightarrow 2HO^\bullet \tag{1}$$

$$2HO^\bullet + 2RH \rightarrow 2H_2O + 2R^\bullet \tag{2}$$

$$\Delta H = 2\Delta H_f(R^\bullet)_{aq} - 2\Delta H_f(RH)_{aq} + 2\Delta H_f(H_2O)_{aq} - \Delta H_f(H_2O_2)_{aq} \tag{3}$$

measurement of the combined heats of reactions 1 and 2, it was imperative that the lifetime of R$^\bullet$ was long compared to the microphone response and that reactions 1 and 2 were completed in a time that was short with respect to that response.

The first condition was easily achieved by attenuating the laser flux so that radical concentrations were low, which limits radical–radical reactions. We have previously established[11] that, under our experimental conditions, lifetimes of R$^\bullet$ were of the order of milliseconds so that heats of reactions associated with radical decay did not contribute to the photoacoustic signal.

Fulfilling the second condition requires a thorough knowledge of the rate constants for reaction 2. Fortunately, an extensive body of data for the reactions of hydroxyl radicals is available from pulse-radiolysis studies. For most of the substrates used in this work (Table I), rate constants, k_2, are ca. 10^9 M^{-1} s^{-1} [12] and at the concentrations of substrates used (3.2–7.6 M) reactions 1 and 2 must have been complete in a time that was very short with respect to the response of our fastest detector (0.2 μs). This was checked by varying the concentrations of the substrates and by demonstrating that the measured heats of reaction were independent of substrate concentration. However, the reactions of hydroxyl with two of the substrates—acetonitrile and acetate ion—were slow by comparison ($k_2 = 2.2 \times 10^7$ and 8.5×10^7 M^{-1} s^{-1}, respectively)[13,14] and required the use of the slower detector (2 μs) and high concentrations of substrate ([CH_3CN] = 5.7 M, [CH_3CO_2H] = 5.2 M).

Table I. Heats of Reactions 1 and 2 (kcal mol^{-1}) Measured at 300 K in Water

substrate	ΔH_{aq}^{obs} [a]	$\Delta H(CH)_{aq}$ [a]	$\Delta H(CH)_g$, [b] lit	$\Delta H(CH)_g$, this work
$\underline{C}H_3OH$	−9.6 ± 0.7	−11.4 ± 0.7	1 ± 3	−3.5 ± 0.7
$CH_3\underline{C}H_2OH$	−8.0 ± 1.2	−10.7 ± 1.2	−1 ± 2	−2.8 ± 1.2
$(CH_3)_2\underline{C}HOH$	−13.2 ± 0.7	−16.4 ± 0.7	−5 ± 2	−8.5 ± 0.7
$(\underline{C}H_3)_3COH$	3.6 ± 1.0	3.1 ± 1.0	13 ± 3	11.0 ± 1.0
$(\underline{C}H_2OH)_2$	−16.0 ± 1.2	−16.0 ± 1.2	−10 ± 2 [c]	−8.1 ± 1.2
$\underline{C}H_3CN$	−6.2 ± 0.7	−4.2 ± 0.7	−1 ± 4	3.7 ± 0.7
$\underline{C}H_3COO^-$	−11.6 ± 0.7	−11.3 ± 0.7		−3.4 ± 0.7

[a] For details of correction, see Appendix 1. [b] Reference 4 and 18. [c] Private communication, Lossing, F. P.

The combined heats of reactions 1 and 2 were obtained by measuring the amplitude of the signal from the transducer as the concentration of hydrogen peroxide was varied over the range (0.3–1.75 M). The signal amplitude was corrected for any variations in the laser power and this *normalized* response was plotted against the fraction of laser light absorbed by the hydrogen peroxide. In general, hydrogen peroxide was the only compound present that absorbed at the laser wavelength and the plots were all straight lines that passed through the origin. The photoacoustic cell was then cleaned and solutions of the standard (generally 2,4-dihydroxybenzophenone) were introduced. Again, plots of the normalized photoacoustic response versus the fraction of light absorbed by the standard were straight lines that passed through the origin.

The 2,4-dihydroxybenzophenone converted all of the light that it absorbed into heat within a few nanoseconds[15] and therefore completely transformed the light energy into heat in a time that was very short compared to the detector response. Under these conditions, the heat evolved in reactions 1 and 2, ΔH_{aq}^{obs}, was given by eq 4, where a_r and a_s were the slopes of the plots for the mixture

$$\Delta H_{aq}^{obs} = (84.8/\Phi)(1 - a_r/a_s) \text{ kcal mol}^{-1} \tag{4}$$

and standard, respectively, Φ was the quantum yield for hydrogen peroxide photolysis,[16] and 84.8 kcal mol^{-1} represents the laser energy. The measured heats of reaction are reported in Table I.

Hydroxyl radicals react with the substrates under investigation with a high degree of regiospecificity (>85% at the $\underline{C}H$ site; Table I).[12-14] Indeed, the substrates were deliberately selected with this property in mind. However, small corrections to the thermochemistry needed to be made that reflected hydroxyl radical attack at the less important positions or at hydrogen peroxide. Details of these corrections are given in Appendix 1. In general the corrections were very small and were of the order of the experimental errors, ca. ±1 kcal mol^{-1}. Table I shows the revised heats of reactions 1 and 2, $\Delta H(\underline{C}H)_{aq}$, that account for the small contributions due to the lack of perfect regiospecificity.

Our aim, in this work, was to see how the use of a very polar solvent, water, might affect the thermochemistry of free-radical reactions. Accordingly, we calculated the heats of reactions 1 and 2 with gas-phase data (Table I). A cursory glance at the data immediately shows that there is poor agreement between the

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solution-phase and gas-phase data notwithstanding the experimental errors. However, it is noteworthy that the solution-phase results seem to be consistently ca. 5–10 kcal mol^{-1} lower than the gas-phase data. This observation suggested that a small solvent effect might be operative but what was its origin?

In eq 1 and 2 we are converting an organic compound to its corresponding free radical and are changing a molecule of hydrogen peroxide into two of water. We therefore decided to deal with each of these transformations separately and to see if existing literature data indicated the presence of a solvent effect on one or both.

Looking first at the transformation of hydrogen donor to its corresponding radical, literature data suggests that solvent effects on this reaction may not be substantial. It has already been thoroughly established that measurements of bond strengths in nonpolar solvents[6,11] lead to data that are in excellent accord with gas-phase results. Indeed, solution experiments on the heats of formation of simple alkyl radicals[6] correctly established that the contemporary gas-phase values were too low and paved the way for revision to the latter.[4,5] Moreover, recent experiments[9] on the interaction of capto-dative stabilized radicals with polar solvents suggest that there is little gain in solvation energy when a nonpolar substrate is dissociated into two radicals that have substantial dipole moments. However, we feel that the most compelling evidence against there being a substantial solvent effect on the RH to R$^\bullet$ transformation comes from ionic chemistry.

With use of the data for the oxidation potentials of free radicals in solution,[17] it has become possible to calculate the bond-dissociation energies for radical cations in solution and to compare these with gas-phase results (eq 5). Although only limited data are

$$\mathrm{R}\overset{+}{-}\mathrm{R} \rightarrow \mathrm{R}^\bullet + \mathrm{R}^+ \tag{5}$$

available (R = benzyl and R = CH_2NH_2), the gas-phase data and solution data (acetonitrile solvent) for the heats of reaction 5 agreed within experimental error. This implied that, even when there was a substantial change in structure for the charge-carrying species as a result of the dissociation, there was little difference in the solvation energies. If this is true for charged species in polar solvents, it is likely to be true for the transformation of nonpolar structures, i.e. of RH to R$^\bullet$.

Additional supporting evidence comes from electrochemical results that led to data for the free energies of the heterolytic cleavage of hydrocarbons in acetonitrile and dimethylsulfoxide (eq 6). In the three cases where data were available,[17] R = benzyl,

$$\mathrm{RH} \rightarrow \mathrm{R}^- + \mathrm{H}^+ \tag{6}$$

diphenylmethyl, and fluorenyl, the differences in the free energies of reaction 6 in going from acetonitrile to dimethylsulfoxide as solvent were ca. −15.6 kcal mol^{-1}, which corresponded to the change in solvation energy for the proton between the two solvents. Again the result implied that, for the large organic ions, solvation energies varied little in going from one polar solvent to another and that the major change in solvation was attributable to the very small charged species, the proton.

With these results in mind, we can look at reactions 1 and 2 and we can begin with the hypothesis that the transformation of RH to R$^\bullet$ leads to little change in solvation energy. We can then estimate the effect of the remaining transformation in which a hydrogen peroxide is destroyed and two molecules of water are formed.

Literature data on the heats of solvation of hydrogen peroxide and water[18] indicate that the heat evolved in this process is 7.9 kcal mol^{-1} greater in water than in the gas phase. Addition of this quantity to our data for $\Delta H(\underline{C}H)_{aq}$ leads to $\Delta H(\underline{C}H)_g$ (Table I) that correspond, within experimental error, to the heats of reactions 1 and 2 calculated from the gas-phase data. This agreement underscores the correctness of the hypothesis that the difference in the solvation energies of RH and R$^\bullet$ is negligible and that only the solvation of the smaller molecules brought about differences between $\Delta H(\underline{C}H)_{aq}$ and $\Delta H(\underline{C}H)_g$.

Table II. Carbon–Hydrogen Bond-Dissociation Energies (kcal mol^{-1}) in Water and in the Gas Phase

substrate	BDE_{aq},[a] this work	BDE_g,[b] lit	BDE_g,[a] this work
CH_3OH	90.9 ± 1.7	94 ± 2	91.9 ± 1.7
CH_3CH_2OH	91.2 ± 2.2	93 ± 1	92.2 ± 2.2
$(CH_3)_2CHOH$	88.3 ± 1.7	91 ± 1	89.3 ± 1.7
$(CH_3)_3COH$	98.1 ± 2.0	100 ± 2	99.1 ± 2.0
$(CH_2OH)_2$	88.6 ± 2.2	91 ± 1[c]	89.6 ± 2.2
CH_3CN	94.5 ± 1.7	93 ± 2.5	95.5 ± 1.7
CH_3COO^-	90.9 ± 1.7		91.9 ± 1.7

[a] Errors stated include a contribution of ±1 kcal mol^{-1} due to uncertainties in $\Delta H_f(H_2O_2)_{aq}$ and $\Delta H_f(H_2O)_{aq}$. [b] Reference 4. [c] Lossing, F. P., private communication.

We made use of the measured heats of reactions 1 and 2 to calculate bond-dissociation energies, BDE(RH), for the substrates in question (eq 7, 8) and again made use of the heats of formation

$$\mathrm{BDE(RH)}_{aq} = \Delta H_f(\mathrm{R}^\bullet)_{aq} + \Delta H_f(\mathrm{H}^\bullet)_{aq} - \Delta H_f(\mathrm{RH})_{aq} \tag{7}$$

$$\mathrm{BDE(RH)}_{aq} = \Delta H(\underline{\mathrm{C}}\mathrm{H})_{aq}/2 + \Delta H_f(\mathrm{H}^\bullet)_{aq} - \Delta H_f(\mathrm{H_2O})_{aq} + \Delta H_f(\mathrm{H_2O_2})_{aq}/2 \tag{8}$$

of hydrogen peroxide, water, and the hydrogen atom that apply in water.[18,19] Combining these data led to the relationship shown in eq 9. The bond-dissociation energies are reported in Table II together with the corresponding gas-phase values.

$$\mathrm{BDE(RH)}_{aq} = \Delta H(\underline{\mathrm{C}}\mathrm{H})_{aq}/2 + 96.6\ \mathrm{kcal\ mol^{-1}} \tag{9}$$

We have already established that there was little or no difference between the heats of solvation of molecules RH and their corresponding radicals R$^\bullet$. The implication of this finding is that the CH bond-dissociation energies in water and the gas phase will differ only by the heat of solvation of the hydrogen atom (−1 kcal mol^{-1}), which is similar to the experimental error. The data in Table II illustrate this point and offer another perspective on the experimental results. They support the general conclusion that it is the solvation energies of the small and polar components of a reaction that are far more important than the solvation energy differences between RH and R$^\bullet$. For completeness, we have included $\mathrm{BDE(RH)}_g$ that were calculated from our solution data by correcting for the solvation of the hydrogen atom alone (Table II).

The conclusions drawn from these experiments can be combined with those associated with experiments carried out in nonpolar solvents to establish some simple guidelines that relate solution and gas-phase thermochemistry for free-radical processes.

Guidelines

1. Heats of free-radical reactions will be the same in nonpolar solvents and the gas phase. This is because *differences* in the solvation energies of radicals and their parent molecules are minimal.

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(19) (a) The volume changes associated with reactions 1 and 2 are so small that the pressure–volume working which they contribute to the reaction energy is negligible when compared to the enthalpy change. Nevertheless, it is arguable that these volume changes could contribute to the solvent expansion that gives rise to the photoacoustic effect. In experiments with hydrocarbon solvents,[11] the excellent agreement between photoacoustic and literature data suggests that such effects are minimal in organic solvents. While water[19b] has a smaller coefficient of thermal expansion (0.23 × 10^{-3} mL deg^{-1}) at 20 °C than say isooctane[19c] (1.70 × 10^{-3} mL deg^{-1}), it should be noted that the solutions used in this work often contained up to 30% of an organic substrate which would have significantly reduced these differences; e.g. for 30% isopropyl alcohol in water[19d] the coefficient of thermal expansion is 0.698 × 10^{-3} mL deg^{-1}. (b) Stott, V.; Bigg, P. H. In *International Critical Tables*, Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. III, p 24. (c) Pomerantz, P. *J. Res. Natl. Bur. Stand.* **1952**, *48*, 76. (d) Bearce, H. W.; Mulligan, G. C.; Maslin, M. P. In *International Critical Tables*, Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. III, p 115.

2. Heats of free-radical reactions in polar solvents will differ from those in the gas phase to an extent that reflects the solvation energies associated with the net formation or destruction of very polar species. The solvation energies of structurally related reagent and product molecules, e.g. a hydrocarbon and its corresponding radical, will be similar and their contributions to the overall thermochemistry will tend to cancel.

3. Bond-dissociation energies are themselves heats of specific reactions and guidelines 1 and 2 will apply in those cases.

These guidelines are as reliable as the experiments on which they were based, i.e. ± 1–2 kcal mol^{-1}.

Summary

Measurements, in water, of the heats of reaction of hydrogen peroxide with a variety of organic substrates led to data that were within 5–10 kcal mol^{-1} less than their gas-phase equivalents. The difference between the two sets of data was not associated with a special solvation of the radicals that were the reaction products. In fact, the difference was due to the change in the enthalpy of solvation that occurred when 1 equiv of hydrogen peroxide was converted to 2 of water during the course of the reaction.

The results imply that solvent effects on the conversion of organic molecules (RH) to their corresponding free radicals ($R^\bullet$) are very small and that, to a good approximation, gas-phase data can be applied directly to solution work, even when polar solvents are being used. Gas-phase and solution data for heats of reaction can be completely unified if account is taken of changes in solvation energies for small, polar molecules that participate.

Appendix 1. Corrections to ΔH_{aq}^{obs}

The reactions of hydroxyl radicals with the substrates under investigation show a high degree of regioselectivity.[12-14] However, corrections to ΔH_{aq}^{obs} were required that reflected the extent of attack at the sites of minor importance.

If hydrogen abstraction occurs at a minor site, i, in the substrate, then the molar heat of reaction at that site is defined by eq 10. For convenience, this can be recast in terms of the strength of the ith bond in the molecule, eq 11.

$$\Delta H_{aq}^{i} = 2\Delta H_f(R^{i\bullet})_{aq} - 2\Delta H_f(RH)_{aq} + 2\Delta H_f(H_2O)_{aq} - \Delta H_f(H_2O)_{aq} \quad (10)$$

$$\Delta H_{aq}^{i} = 2BDE(R^iH)_g - 2\Delta H_f(H^\bullet)_g + 2\Delta H_f(H_2O)_{aq} - \Delta H_f(H_2O_2)_{aq} \quad (11)$$

To make the corrections we used the heats of formation of water and hydrogen peroxide in aqueous solution (−68.3 and −45.7 kcal mol^{-1}, respectively)[18] and gas-phase data for the strengths of the bonds at the sites of minor reaction. We believe that this use of gas-phase data is valid because the corrections themselves are small and are of the order of the experimental errors. Moreover, any contribution to the correction from solvent effects must reflect differences in the solvation energies of RH and $R^{i\bullet}$ which are likely to be minimal.

Table III. Corrections to the Heats of Reactions 1 and 2 Due to Hydrogen Abstraction at Minor Sites in the Substrate Molecules

substrate	site	f^i	BDE(R^iH),[a] kcal mol^{-1}	C, kcal/mol^{-1}
CH_3OH^1	1	0.07	104.4	0.96
$CH_3^1CH_2OH^2$	1	0.132	100.1[b]	1.0
	2	0.025	104.2	
$(CH_3^1)_2CHOH^2$	1	0.133	100.1[b]	0.85
	2	0.012	104.7	
$(CH_3)_3COH^1$	1	0.043	105.1	0.65
$(CH_2OH^1)_2$	1	<0.001	104.2[c]	0.0
CH_3CN	*d*	0.136[e]	88.2[f]	−2.57
CH_3COO^-	*d*	0.043[e]	88.2[f]	−0.81

[a] Reference 4. [b] Reference 5. [c] Assumed to be equal to BDE(CH_3CH_2O–H). [d] Competitive abstraction from H_2O_2. [e] Fraction of attack at H_2O_2; ref 13 and 14. [f] BDE(HOO–H), ref 18 and Shum, L. G. S.; Benson, S. W. *J. Phys. Chem.* **1983**, *87*, 3479.

Clearly, the contribution due to hydrogen abstraction at minor sites must be weighted by the fraction of attack at the site, f^i, and must then be combined with contributions from the other minor sites so as to produce a global correction, C (eq 12). It

$$C = \sum_i \Delta H_{aq}^i f^i \quad (12)$$

should be noted that this equation deals only with the minor sites and does not include any contribution from the major site of reaction, $\underline{C}H$ (Table I). We deliberately cast the equations in this way so that the corrections were cleanly separated from the main thermochemistry. This formulation allows the magnitude of the corrections to be compared with heats of reaction, bond-dissociation energies, and the experimental errors.

Details of the calculations are given in Table III. The corrected heats of reaction at the major sites, $\Delta H_{aq}(\underline{C}H)$, are then given by eq 13

$$\Delta H(\underline{C}H)_{aq} = (\Delta H_{aq}^{obs} - C)/(1 - \sum_i f^i) \quad (13)$$

where ΔH_{aq}^{obs} were the heats of reaction measured in the photoacoustic experiments. The observed and corrected values of ΔH_{aq} are reported in Table I.

Registry No. $HO^\bullet$, 3352-57-6; CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_3COH$, 75-65-0; $(CH_2OH)_2$, 107-21-1; CH_3CN, 75-05-8; CH_3COO^-, 71-50-1.