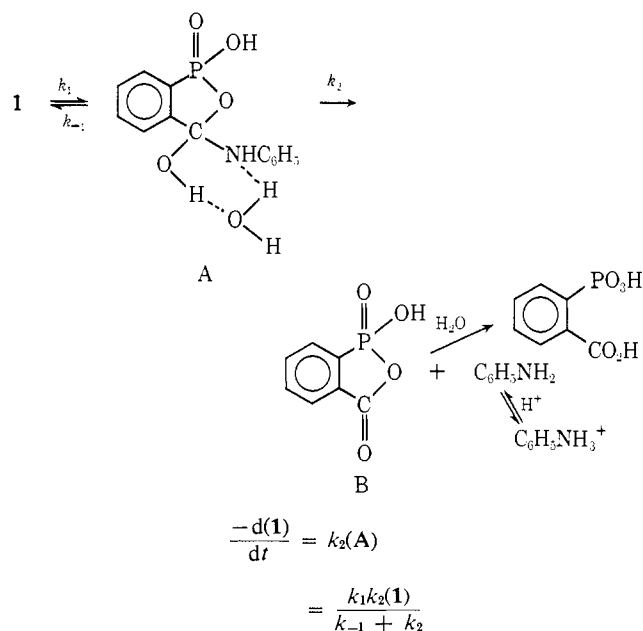


ciated with **1'**,  $k_{\text{obsd}}$  exceeds the extrapolated  $k_{\text{obsd}}$  for benzanilide by a factor of  $6 \times 10^5$ . The rate constant for the bimolecular reaction between phosphate and **3** is very small. No reaction of **3** in 1 M potassium phosphate buffer (pH 6) was observed when the solution was maintained at 90° for 1 month. Therefore, comparison of the rate of the intramolecular reaction of the internal phosphonate residue with the amide with that of external phosphate and **3** can only be estimated to favor the internal reaction by an apparent concentration of more than  $10^3$  M, assuming we could detect a concentration change of 3%. The solvent isotope effect in both plateau regions (below pH 2 and above pH 5),  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$ , is 1.0, indicative of nucleophilic catalysis.<sup>7</sup>

We propose the mechanism in Scheme I as a likely

Scheme I



Therefore  $k$  in eq 1 =  $\frac{k_1 k_2}{k_{-1} + k_2}$

route for the hydrolysis reaction of **1** which is consistent with the experimental data and kinetic forms (an analogous route can be written for the monoanion). The proposed cyclic acyl phosphonate intermediate (**B**) is a compound known to hydrolyze rapidly under the conditions of the amide hydrolysis reaction.<sup>8,9</sup> In Scheme I, hydrolysis of the acyl phosphonate **B** occurs after the aniline molecule has left the addition intermediate and thus after the chromophore being observed has been eliminated.

Nucleophilic catalysis by neighboring un-ionized carboxyl functions (or the zwitterionic equivalent) is a favored mechanism in the hydrolysis of amides<sup>10-16</sup>

although a mechanism involving electrostatic catalysis has also been considered.<sup>12,14,16</sup> The observed rate constant for hydrolysis of these compounds shows a plateau region similar to that which we have observed for **1**, where the plateau ends as dissociation of the carboxylic acid occurs. Solvent isotope effects on these rate constants for carboxyl participation are also near unity. This argues for a similarity of mechanism between the phosphoric and carboxylic acid cases. Since dissociation of the proton from the phosphonate monoacid occurs at higher pH than does the corresponding carboxylic acid, the phosphonate group is an apparently more effective internal catalyst in neutral solution. Our finding further emphasizes that the amide functionality is reactive toward noncarboxylic functional groups as well as carboxylic acids. The very large rate ratio of the inter- and intramolecular reactions of phosphate with the amide gives further indication of a mechanism involving nucleophilic rather than general acid or base catalysis.<sup>17</sup>

We are examining the requirements for interaction of phosphates and amides in further detail and are extending our kinetic studies on these and related systems.

**Acknowledgments.** We note our appreciation for support provided by the National Institute of Arthritis, Metabolism and Digestive Diseases (AM-15013-03) and the Research Corporation.

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## Experimental Solvation Energies of Aliphatic Alkoxide Ions and Hydroxide Ions

Sir:

We wish to report here (for the first time to our knowledge) the relative solvation enthalpies for a series of aliphatic alkoxide ions and hydroxide ion from the gas phase to dimethyl sulfoxide (DMSO). Several years ago Brauman and Blair<sup>1</sup> demonstrated that the gas-phase order of acidity for a few common aliphatic alcohols is exactly the reverse of that reported previously from condensed phase studies. The inescapable conclusion is that the observed acidity order for aliphatic alcohols (and presumably some others) in solution is determined primarily by solvation factors. It has been realized for many years that a quantitative evaluation of solvation energies would be practical if only accurate gas-phase equilibrium constants for ion-molecule reactions were available. Recent advances in mass spec-

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Table I. Thermochemical Data for Deprotonation of Alcohols in the Gas Phase and in DMSO Solution

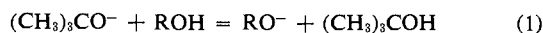
	$\Delta H_D^{\text{DMSO}}$	$\delta\Delta H_D^{\text{DMSO}}$	$\Delta H_D^{\text{g}^a}$	$\delta\Delta H_D^{\text{g}}$	$\Delta H_{\text{S}^{\text{g-DMSO}}}$	$\delta\Delta H_{\text{S}^{\text{g-DMSO}}(\text{ROH})}$	$\delta\Delta H_{\text{S}^{\text{g-DMSO}}(\text{RO}^-)}$
1. $\text{CH}_3\text{OH}$	$-16.0 \pm 0.3$	$-6.8 \pm 0.50$	376.8	$4.1 \pm 0.2$	$-9.25 \pm 0.06$	$-0.09 \pm 0.12$	$-11.0$
2. $\text{C}_2\text{H}_5\text{OH}$	$-11.1 \pm 0.4$	$-1.9 \pm 0.57$	374.9	$2.2 \pm 0.2$	$-9.82 \pm 0.03$	$-0.67 \pm 0.10$	$-4.8$
3. $(\text{CH}_3)_2\text{CHOH}$	$-9.5 \pm 0.2$	$-0.3 \pm 0.45$	373.5	$0.8 \pm 0.2$	$-9.94 \pm 0.04$	$-0.78 \pm 0.11$	$-1.9$
4. $(\text{CH}_3)_3\text{COH}$	$-9.2 \pm 0.4$	(0.0)	372.7	(0.0)	$-9.16 \pm 0.10$	(0.0)	(0.0)
5. $(\text{CH}_3)_3\text{CCH}_2\text{OH}$	$-10.6 \pm 0.4$	$-1.4 \pm 0.57$	371.4	$-1.3 \pm 0.2$	$-10.50 \pm 0.30$	$-1.34 \pm 0.32$	1.4
6. $[(\text{CH}_3)_3\text{C}]_2\text{CHOH}$	$-7.5 \pm 0.3$	$1.7 \pm 0.50$	369.7	$-3.0 \pm 0.3$	$-12.17 \pm 0.21$	$-3.01 \pm 0.23$	1.7
7. $[(\text{CH}_3)_3\text{C}]_3\text{COH}$			366.7	$-6.0 \pm 1.0$			
8. $\text{H}_2\text{O}$	$-12.2 \pm 0.2$	$-3.2 \pm 0.45$	390 <sup>b</sup>	17.3	$-11.79^c \pm 0.01$	$-2.63 \pm 0.10$	$-23.13$

$$\delta\Delta H_D^{\text{DMSO}} = \Delta H_D^{\text{DMSO}}(\text{ROH}) - \Delta H_D^{\text{DMSO}}(t\text{-BuOH}); \delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{RO}^-) = \delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{ROH}) + \delta\Delta H_D^{\text{DMSO}} - \delta\Delta H_D^{\text{g}}$$

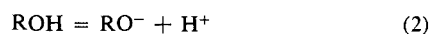
<sup>a</sup> Absolute values of  $\Delta H_D^{\text{g}}$  are references to HF at 371.3 kcal/mol. All relative ( $\delta$ ) values are based on *tert*-butyl alcohol and *tert*-butoxide ion for  $(\text{CH}_3)_3\text{CO}^- + \text{ROH} = \text{RO}^- + (\text{CH}_3)_3\text{COH}$ . <sup>b</sup> D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, U. S. Department of Commerce, NSRDS-NBS, No. 37 (1971). <sup>c</sup> I. Wadsö, *Acta Chem. Scand.*, **20**, 536 (1966).

trometry now make this possible<sup>2</sup> and we have applied them here.

In Table I are presented the necessary thermochemical data to compare heats of deprotonation<sup>3</sup> ( $\Delta H_D^{\text{DMSO}}$ ) of the alcohols and water by a dimethyl sulfoxide (DMSO) solution of its potassium salt (DMSYL) with corresponding gas-phase data ( $\Delta H_D^{\text{g}}$ ). Pulsed ion cyclotron resonance spectroscopy<sup>4-6</sup> was used to measure equilibrium constants for gas-phase proton transfer reactions such as



Since gas-phase acidity may be defined as the free energy change ( $\Delta G^{\circ}_{298}$ ) for the reaction



it is apparent that the free energy change for reaction 1 is a quantitative measure of the acidity of ROH relative to  $(\text{CH}_3)_3\text{COH}$ . By measuring the acidity of the aliphatic alcohols relative to hydrogen fluoride in the gas phase,  $\Delta H_D^{\text{g}}$  can be calculated.<sup>7</sup> Heats of vaporization ( $\Delta H_{\text{vap}}$ )<sup>8</sup> or sublimation of the parent alcohols may be combined directly with  $\Delta H_D^{\text{DMSO}}$  and  $\Delta H_D^{\text{g}}$  values through a simple cycle<sup>2</sup> to obtain the relative enthalpies of solution of the corresponding alkoxide ions [ $\delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{RO}^-)$ ]. The value for water is cited from the JANAF thermochemical tables and was not compared directly with the alcohols under equilibration.

Table I shows clearly the progressively more exothermic enthalpy of deprotonation in the gas phase ( $\delta\Delta H_D^{\text{g}}$ ) as the aliphatic portion of the molecule is elaborated.<sup>9</sup> We believe that this trend is best understood in terms of potential energy changes within the  $\text{RO}^-$  ions due to a charge-induced dipole polarization interaction which increases with the size of the alkyl group.<sup>1</sup> Support for this viewpoint is afforded by the

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(9) In the gas phase the entropy change for reactions of type 1 is very small. The relative enthalpies of deprotonation in the gas phase ( $\delta\Delta H_D^{\text{g}}$ ) are essentially identical, therefore, with the relative free energies of deprotonation ( $\delta\Delta G_D^{\text{g}}$ ). In DMSO the entropies of deprotonation for alcohols 1, 2, 3, and 4 are identical within experimental error ( $\pm 6$  eu, see ref 3).

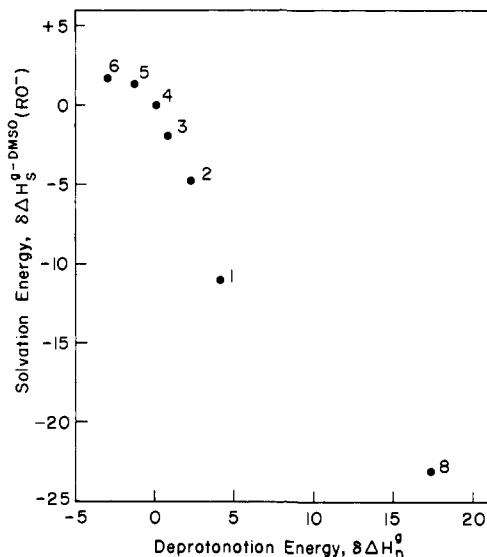


Figure 1. Effects of structural changes on the gas-phase deprotonation energies ( $\delta\Delta H_D^{\text{g}}$ ) and solvation energies [ $\delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{RO}^-)$ ] for water and the aliphatic alcohols in Table I. Units are in kilocalories per mole.

fact that the effects of stabilizing *positive* charges on  $\text{RNH}_3^+$  relative to  $\text{NH}_4^+$  are quantitatively similar to those found here for stabilizing  $\text{RO}^-$  relative to  $\text{OH}^-$ . The more exact analogy of  $\text{ROH}_2^+$  relative to  $\text{H}_3\text{O}^+$  is presently under study in our laboratories.

An opposite trend is shown for the corresponding solvation enthalpies [ $\delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{RO}^-)$ ]. In fact, as Figure 1 shows, a fair ( $R = 0.94$ ) correlation holds between the effects of structural change on the two properties for  $\text{RO}^-$  ions. Aue<sup>10</sup> has reported a similar relationship for ammonium ions. The solvation energy is considerably more sensitive to increasing the size of the alkyl group than is the gas-phase stabilization energy.

Clearly the solvation energies of the entire series are related inversely to their sizes. This relationship is consistent with Born charging "continuum" solvation. A plot of  $\delta\Delta H_{\text{S}^{\text{g-DMSO}}}(\text{RO}^-)$  values from Table I vs. the crude reciprocal radius (estimated from the cube root of the molar volume) has a correlation coefficient of 0.9989.

Steric hindrance to ion-pairing or ion-dipole interactions, specifically in the neighborhood of the oxygen

(10) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

atom, could also be involved. Exner and Steiner<sup>11</sup> have reported sufficient data to suggest that the potassium *tert*-butoxide formed from reference alcohol 4 could be about half associated and that the methoxide salt would be more so. Likewise, we find strong indications of ion pairing from effects of cation variation on  $\Delta H_D^{\text{DMSO}}$  in our system. We are thus unable at this time to describe the respective roles of counterion and solvent in determining what we have referred to grossly as solvation energies.

In the course of a systematic extension of this structure-reactivity study of about 20 alcohols, we have found that  $\Delta H_D^{\text{DMSO}}$  correlates rather well with Taft's  $\sigma^*$  aliphatic substituent constants. The deprotonation reaction becomes progressively less exothermic as the aliphatic bulk of ROH is developed in conformity with previous studies of alcohol acidities in solution<sup>11</sup> but contrary to results in the gas phase. This has the important implication that in this series of compounds the correlation of  $\Delta H_D^{\text{DMSO}}$  with  $\sigma^*$  is determined primarily by changes in solvation energy rather than changes in the gas-phase potential energies of ROH or RO<sup>-</sup>.

Tri-*tert*-butylcarbinol was prepared by the method of Bartlett and Lefferts<sup>12</sup> and di-*tert*-butylcarbinol by LiAlH<sub>4</sub> reduction of di-*tert*-butyl ketone. Neopentyl alcohol was commercial material (Aldrich).

All three solid alcohols were triply sublimed to give melting points in agreement with literature values and provided spectra, both pmr and ir, supporting their structures. Evidence that clean deprotonation occurred was obtained from pmr spectra of the alkoxide solutions which were identical with those of the alcohols in every way save for the absence of an OH peak.<sup>13</sup>

Completeness of deprotonation is suggested, but not proved, by the reported  $pK_a$ 's<sup>14</sup> (28.3–29.2) in this medium whose  $H^-$  is about 33. Also, it was shown routinely that the observed heats of deprotonation in the working range of 10<sup>-3</sup> to 10<sup>-2</sup> M were independent of alcohol concentration. Thus complications from homoconjugate ion (ROH ··· OR<sup>-</sup>) formation<sup>11</sup> are unlikely.

In this connection the very high solvation energy of hydroxide ion and the very low gas phase acidity of water are intriguing. We have noted elsewhere<sup>2</sup> the low basicity of water and the implied high solvation energy of H<sub>3</sub>O<sup>+</sup> into aqueous media. In view of the very low basicity and acidity of separated water molecules in the gas phase,<sup>15</sup> the high autoprotolysis constant of liquid water implies a remarkable ability of this extraordinary medium to solvate its lyonium and lyate ions. This fact, so essential to biophysical processes, is illustrated here with great force.

(11) See J. H. Exner and E. C. Steiner, *J. Amer. Chem. Soc.*, **96**, 1782 (1974), for discussion and key references.

(12) P. D. Bartlett and E. B. Lefferts, *J. Amer. Chem. Soc.*, **77**, 2804 (1955). Yields were considerably improved by use of tetramethylethylenediamine to complex the lithium ion.

(13) In preliminary discussions of these data we erroneously reported that the large exothermic reaction of tri-*tert*-butylcarbinol was due to deprotonation. This conclusion was based on superimposable pmr spectra of reactants and products but is controverted by a recovery experiment from high dilution. The details of this reaction will be presented in a subsequent report. Alcohols 5 and 6 were completely recoverable.

(14) C. D. Ritchie in "Solute-Solvent Interactions," Marcel Dekker, New York, N. Y., 1969.

(15) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967), have deduced that water is both a very weak acid and base in DMSO.

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(16) Alfred P. Sloan Fellow, 1973–1975.

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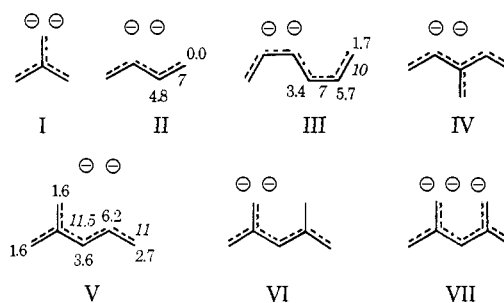
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### Allylic Di- and Trimetalation of Some Simple Alkenes and Dienes<sup>1</sup>

Sir:

Dimetalation of isobutylene gives the Y-shaped dianion I (possibly aromatic<sup>2</sup>).<sup>3</sup> 1,3,6-Cyclononatriene dimetalates to produce homocyclooctatetraene dianion (homoaromatic).<sup>4</sup> To learn whether aromatic or homoaromatic stabilization is required for dimetalation of alkenes, we attempted the preparation of further dianions, including some linear acyclic ones which definitely lack aromaticity. We wish to report the preparation of four new dilithiated species II, III, V, and VI, and one trilithiated substance VII; though



depicted as anions for convenience, these substances may contain at least one covalent carbon-lithium bond.

Metalation was carried out using 2 equiv (three for the preparation of VII) of *n*-butyllithium in 2 equiv of tetramethylethylenediamine (TMEDA) under argon at 25° for 1–4 days. Higher proportions of TMEDA gave less dianion and more TMEDA cleavage products. Conjugated dienes were unsuitable precursors due to competing addition, but monoenes and unconjugated dienes were successfully used. II was prepared from 1-butene and (*Z*)- and (*E*)-2-butenes, showing that an

(1) Presented in part at the First Fall Organic Conference, American Chemical Society, N. Falmouth, Mass., Sept 30, 1973, Abstracts, p 35.

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