rect, but they do not permit one to assess individually the accuracy of the entropy and enthalpy terms used in obtaining the free energy values.

Fineman and Wallace[2] assumed that the entropy of formation of the solid solution between 0 and 350°K. is the entropy of random mixing, while Hovi and Hyvönen[3] based their entropy calculations upon a postulated local order for the solid solution lattice. The enthalpy values used by the latter investigators were also calculated on the basis of their postulated lattice structure, while those used by Fineman and Wallace were determined experimentally on solids prepared by fusion of mixtures of the pure salts. Such experimental enthalpies may not be characteristic of the solid solutions in their equilibrium state at room temperature. In the potassium bromide–potassium chloride system Fontell and co-workers[15] have shown that the enthalpy determined calorimetrically at 25° for a 50 mole per cent. solid solution prepared by fusion is 10 cal. per mole higher than the value determined in the same manner for a preparation obtained by isothermal, isobaric crystallization from water (and therefore more nearly in a state of thermodynamic equilibrium at room temperature[16]). The sensitivity of the free energy iso-

(15) N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennica, Math.-Phys.*, **Ser. A**, 54 (1949).

(16) J. A. Wasastjerna, *Soc. Sci. Fennica Commentationes Phys.-Math.*, **15**, No. 3 (1949).

therms to small changes in the enthalpy values is illustrated by Wallace and Fineman's recalculation[17] of the phase diagram for the potassium bromide–potassium chloride system originally proposed by Fontell[18] on the basis of his measurements of the heats of formation in this system. By choosing an analytical expression for the data which was statistically more satisfactory than the one used by Fontell (thus effectively altering Fontell's enthalpy values by amounts ranging up to 25 cal.) they obtained a critical solution temperature at 240°K. compared to Fontell's calculation of 398°K.

The calculations of both pairs of investigators are probably correct in predicting incomplete miscibility below about 250°K., but the uncertainties in the free energy values (arising from the enthalpy and entropy assumptions) make it difficult to establish with confidence a critical solution temperature. The results of this investigation indicate that, while partial miscibility is to be expected in this system, the critical solution temperature must lie below 308°K.

Acknowledgment.—The authors acknowledge with appreciation the support given to this investigation by the Rutgers University Research Council.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

# The Relative Acidity of Water, Methanol and Other Weak Acids in Isopropyl Alcohol Solution[1]

BY JACK HINE AND MILDRED HINE

The relative acidity of five indicators is determined in isopropyl alcohol solution. By use of one, 4-nitrodiphenylamine, the acidity of about thirty-five alcohols and amides is determined. Methanol is found to be more acidic than water. This, and the decrease in basicity resulting from the successive substitution of alkyl groups for the hydrogen atoms of water is explained in terms of "B-strain" and electronic effects. The relative effect of various R groups on the acidity of several functional groups and the effect of solvent changes on the relative strength of acids are also discussed.

Introduction

In relation to an investigation of the mechanism of the basic hydrolysis of chloroform,[2] it was found that the reaction proceeded much more slowly in methanolic solution than in water or aqueous dioxane. There are several other reactions proceeding by the mechanism

$$HA + B^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftarrows}} A^- + HB$$
$$A^- \xrightarrow{\text{slow}} \text{products}$$
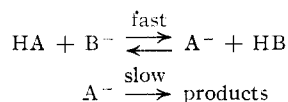
(where B⁻ is the conjugate base of the solvent) described in the literature which are also slowed by the addition of methanol to an aqueous reaction mixture. These include the formation of ethylene

oxide from ethylene halohydrins[3] and the dealdolization of diacetone alcohol.[4] In none of the three cases mentioned is the effect due to the change in dielectric constant, since it is not shared by other low dielectric solvents such as dioxane, t-butyl alcohol and isopropyl alcohol. On the other hand, compounds such as ethylene glycol and glycerol, known to be somewhat more acidic than water,[5] have an effect similar to but somewhat larger than that of methanol. Stephens, McCabe and Warner[3] have suggested that their data may be explained by the postulate that methanol is a stronger acid than water.

By comparing the effect of 1 M methanol on the solubility of calcium hydroxide with its effect on

(1) Presented, in a preliminary form, before the Section on Physical and Inorganic Chemistry of the XIIth International Congress of Pure and Applied Chemistry, New York. N. Y., Sept. 10–13, 1951.

(2) J. Hine, THIS JOURNAL, **72**, 2438 (1950).

(3) J. E. Stevens, C. L. McCabe and J. C. Warner, *ibid.*, **70**, 2449 (1948).

(4) G. Åkerlöf, *ibid.*, **50**, 1272 (1928).

(5) L. Michaelis, *Ber.*, **46**, 3683 (1913); L. Michaelis and P. Rona, *Biochem. Z.*, **49**, 232 (1913).

lead chloride, Faurholt[6] obtained data which, when recalculated by Unmack,[7] indicate that methanol is about six times as strong an acid as water. From conductimetric measurements[7] and a cryoscopic study,[7] Unmack finds methanol to be about three times, and from potentiometric data[8] about twice, as acidic as water. However, calculations based on the autoprotolysis constants of the two compounds are said to indicate that water is about twice as strong an acid as methanol.[9] The composition of the aqueous methanol for which these various values were obtained was not the same in all cases, but it is stated that the values should not vary greatly with the composition. Although it is not obvious why the last value quoted is better than the others, it has been used most commonly by subsequent workers.[10]

Since it was felt that in all of these determinations certain undesirable assumptions were made (usually that a relatively large change in the solvent composition had the same effect on the activity coefficient of the methoxide ion as on that of the hydroxide ion), it was considered worthwhile to attempt the determination of the relative acidity of these and related compounds in a solvent which is a weak enough acid that the concentration of its conjugate base would be decreased detectably by relatively small amounts of water and methanol. The solvent used should be, in addition, as good an ion-solvator as possible and thus preferably a hydroxy compound. For these reasons isopropyl alcohol was chosen. The measurements were carried out by use of the indicator, 4-nitrodiphenylamine, since the measurements of Stearns and Wheland[11] indicated that the acidity of this material should be approximately that desired.

Experimental

Materials.—The solvent used in this work was prepared by distilling $99+\%$ isopropyl alcohol over Drierite and collecting the middle 75% portion. The 4-nitrodiphenylamine was prepared by the method of Lellmann,[12] except that recrystallization (from ethanol) did not give adequate purification and so the material was also sublimed in vacuum. The material used gave no change in its absorption spectrum in either neutral or basic solution upon further recrystallization. The 4,4'-dinitrodiphenylamine was prepared by Lellmann's method[12] without significant modification. The 2,4-dinitrophenylamine, 2,4-dinitroaniline and 4-nitroaniline were commercial products purified by recrystallization (from aqueous ethanol) to constant melting point.

The acids studied were of the highest grade available, in most cases Eastman Kodak Co. white label. The liquids were fractionated (under reduced pressure if it seemed desirable) through a thirty-inch column packed with glass helices and a middle fraction was used. The solids were recrystallized to constant melting points in agreement with those listed in the literature.

The sodium alkoxide solutions were prepared in a drybox, under nitrogen, from freshly cut sodium and were stored under nitrogen.

Acidity Determinations.—The determination of the acidity of 4-nitrodiphenylamine and several related compounds

(6) C. Faurholt, Z. physik. Chem., **126**, 85 (1927).

(7) A. Unmack, ibid., **129**, 349 (1927).

(8) A. Unmack, ibid., **131**, 371 (1928).

(9) A. Unmack, ibid., **133**, 45 (1928).

(10) The resultant value (10^{-16}) for the ionization constant of methanol in aqueous solution has been used, for example, as the basis of the often quoted series of acid strengths determined by W. K. McEwen, THIS JOURNAL, **58**, 1124 (1936).

(11) R. S. Stearns and G. W. Wheland, ibid., **69**, 2025 (1947).

(12) E. Lellmann, Ber., **15**, 825 (1882).

was carried out by a modification of the method of Stearns and Wheland,[11] in which the optical density (at a wave length where the conjugate base of the compound studied is responsible for most of the absorption) of solutions containing known concentrations of compound is measured in the presence of increasing concentrations of base. Solutions of the compounds used were made up by weight on an analytical balance, followed by volumetric dilutions with calibrated pipets. The strength of the sodium isopropoxide solutions used was determined by titration. Immediately after the solutions of sodium isopropoxide and compound were mixed, the optical density was measured in a Beckman quartz spectrophotometer, model DU. The solutions mixed were of such strengths as to give optical density readings in the range 0.3–0.6. Analogous measurements in ethanol solution were made on 4,4'-dinitrodiphenylamine and 4-nitrodiphenylamine.

The strength of the weak acids studied was determined by comparing the optical density of two solutions to which identical concentrations of indicator (4-nitrodiphenylamine) and sodium isopropoxide had been added, but only one of which contained the weak acid. In the procedure used the strengths of two acids were determined simultaneously. The first cell of the spectrophotometer was filled with isopropyl alcohol for use as a blank. To each of three flasks was added an identical volume of the same solution of indicator using the same calibrated pipet. Then by using three pipets whose calibrations showed them to contain within 0.15% of the same volume, a given volume of isopropyl alcohol was added to flask No. 1, of an isopropyl alcohol solution of one acid to flask No. 2 and of another acid to flask No. 3. Then another pipet was used to add a given volume of sodium isopropoxide solution to each of the three flasks. As soon as the flasks were shaken their contents were transferred to the other three spectrophotometer cells and their optical densities determined. The final solutions were about 10^{-4} M in indicator, about 25×10^{-4} M in sodium isopropoxide, and around 0.004 to 0.1 M in the weak acid, depending upon its strength. All measurements were made at $27 \pm 3°$; no differences were detected in results obtained throughout this range.

Data

Determination of the Acidity of 4-Nitrodiphenylamine and Related Compounds.—Stearns and Wheland[11] have shown that if the absorption of a solution of indicator is measured at a wave length at which the conjugate base of the indicator absorbs, but the undissociated indicator does not, and if the concentration of indicator used is negligible compared to the concentration of base, then

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon_{In^-}} + \frac{1}{[OR^-]_0}\left(\frac{1}{\epsilon_{In^-}K_I}\right) \qquad (1)$$

where, at the wave length used, ϵ_{In^-} is the molecular extinction coefficient of the conjugate base of the indicator, ϵ' is called the *apparent extinction coefficient* and is equal to the optical density divided by the formal concentration of indicator, $[OR^-]_0$ is the concentration of base originally added to the solution, and for the equilibrium

$$\text{HIn} + \text{OR}^- \rightleftharpoons \text{In}^- + \text{ROH}$$
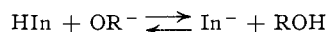
$$K_I = [In^-]/[HIn][OR^-]$$

From equation (1) it may be seen that if ϵ' is determined at a number of different concentrations of OR^-, then a plot of the reciprocal of ϵ' against the reciprocal of $[OR^-]_0$ will yield a straight line with intercept $1/\epsilon_{In^-}$ and slope $1/\epsilon_{In^-} \cdot K_I$. By plots of this sort, Stearns and Wheland determined ϵ_{In^-} and K_I for several weak acids in ethanol solution.

In the present work, in order to use as dilute solutions of indicator as possible, it was desirable to make measurements near the absorption maximum for the indicator anion, even when the indicator itself absorbed appreciably at this wave length. When equation (1) is modified by correcting ϵ' for absorption due to undissociated indicator and $[OR^-]_0$ for that amount of base which reacts with the indicator, equation (2) is obtained

$$\frac{1}{\epsilon' - f\epsilon_{HIn}} = \frac{1}{\epsilon_{In^-}} + \frac{1}{([OR^-]_0 - [In^-])}\left(\frac{1}{\epsilon_{In^-}K_1}\right) \qquad (2)$$

ϵ_{HIn} is the molecular extinction coefficient of the undissociated indicator and f is the fraction of indicator in its undisso-

ciated form. Since the corrections introduced were small in all cases studied, equation (2) may be plotted by successive approximations of the value of f (from which both corrections may be calculated). The graphs obtained for 4-nitrodiphenylamine and for 2,4-dinitroaniline are shown in Fig. 1.
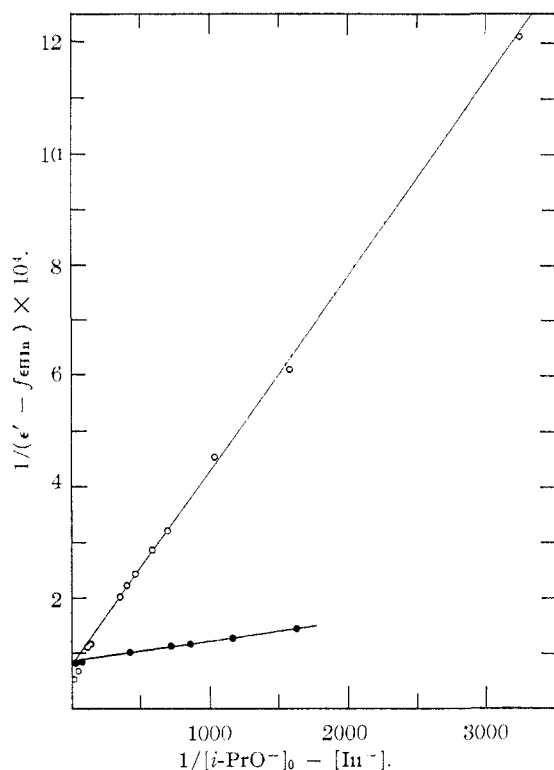

Fig. 1.—Plots of equation (2): O, 4-nitrodiphenylamine; ●, 2,4-dinitroaniline.

While satisfactory straight lines are obtained in dilute sodium isopropoxide solution there are definite deviations (especially in the case of 4-nitrodiphenylamine) in the more concentrated solutions (such a deviation was found by Stearns and Wheland[11] for 2,4-dinitroaniline in ethanol). However, for sodium isopropoxide concentrations in the vicinity of 2×10^{-3}, those used in determining the acidity of the weak acids studied, the agreement is excellent. It is thought that the deviations in more concentrated sodium isopropoxide solutions are due to the formation of ion pairs which absorb more strongly than do the completely dissociated anions.

Values of K_1 were also obtained for 2,4-dinitrodiphenylamine in isopropyl alcohol solution and for 4,4'-dinitrodiphenylamine in both isopropyl alcohol and ethanol solutions. The resultant data are shown in Table I. Measurements were also made on 4-nitrodiphenylamine in ethanol solution,

TABLE I

ACIDITY OF INDICATORS IN ISOPROPYL ALCOHOL

Compound	Wave length, Å.	$\epsilon_{In}^{-} \times 10^{-4}$	K_1
4-Nitrodiphenylamine	5000	1.21	236
2,4-Dinitroaniline	5200	1.15	2700
2,4-Dinitrodiphenylamine	5200	1.50	19,600
4,4'-Dinitrodiphenylamine	5700	4.89	21,600
4,4'-Dinitrodiphenylamine[a]	5700	4.0	43.4

[a] In ethanol solution.

but as found by Stearns and Wheland,[11] the line obtained in the plot of equation (2) passed so close to the origin that no accurate determination of ϵ_{In}^{-} and hence of K_1

could be made. The least-squares equation for the data of Stearns and Wheland gave the value of ϵ_{In}^{-} as: 4.38×10^4 at 5750 Å. and K_I as 3.453×10^{-2}. For K_I we get values of 1.28 and 0.60 by assuming that ϵ_{In}^{-} has the same value in ethanol that it does in isopropyl alcohol and t-butanol, respectively. From Table II it may be seen that an assumption of this sort is not entirely unwarranted, since the values of ϵ_{In}^{-} do not tend to change greatly with

TABLE II

EFFECT OF SOLVENT ON VALUE OF ϵ_{In}^{-} FOR SEVERAL INDICATORS

Compound	Wave length, Å.	EtOH $\times 10^{-4}$	ϵ_{In}^{-} in i-PrOH $\times 10^{-4}$	t-BuOH $\times 10^{-4}$
4,4'-Dinitrodiphenylamine	5700	4.0	4.89	5.30[b]
2,4-Dinitrodiphenylamine	5200	1.35[a]	1.50	1.15[b]
2,4-Dinitroaniline	5200	1.1[a]	1.15	1.30[b]
4-Nitrodiphenylamine	5000		1.21	2.55[b]

[a] Estimated from the data of Stearns and Wheland.[11] [b] The values were determined by measurement in both 0.01 and 0.001 M potassium t-butoxide solutions.

the solvent. Stearns and Wheland's value of ϵ_{In}^{-} at 5750 Å. for 4-nitrodiphenylamine in ethanol corresponds to a value of about 4.5×10^5 at 5000 Å. which seems rather high. By assuming the same solvent effect on this compound as is found on closely related compounds (see Table V) a value of K_1 around 0.4 is obtained. Any of these other values of K_1 seem (from a visual estimate) to fit the data of Stearns[13] as well as his own.

By assuming that at the absorption maximum for its conjugate base (around 4500 Å.) 4-nitroaniline has a value of ϵ_{In}^{-} (1.5×10^4) in the vicinity of those for related indicators for which ϵ_{In}^{-} was determined, we may calculate that in isopropyl alcohol this compound has a K_I around 0.4.

Determination of Relative Strength of Other Weak Acids. —For the other weak acids studied

$$K_e = [A^-]/[HA][i\text{-}PrO^-]$$

was determined[14] by measuring the optical density of two solutions to which identical concentrations of 4-nitrodiphenylamine and sodium isopropoxide had been added and which differed only in that one contained a certain concentration of the acid to be measured.

If the subscripts, final and init., respectively, refer to the solutions with and without the acid, HA, and if D is the optical density, K_1 is the value of K_e for the indicator,

$$[HIn]_{formal} = [HIn] + [In^-], \text{ and } [HA]_{formal} = [HA] + [A^-]$$

then

$$[i\text{-}PrO^-]_{init} = \frac{D_{init} - \epsilon_{HIn}[HIn]_{formal}}{K_1([HIn]_{formal}\epsilon_{In}^- - D_{init})}$$

$[i\text{-}PrO^-]_{final}$ may be equated analogously, and

$$K_e = \frac{[i\text{-}PrO^-]_{init} - [i\text{-}PrO^-]_{final} - [In^-]_{init} + [In^-]_{final}}{([HA]_{formal} - [i\text{-}PrO^-]_{init} + [i\text{-}PrO^-]_{final} - [In^-]_{init} + [In^-]_{final})[i\text{-}PrO^-]_{final}}$$

Except for a few cases where HA is a relatively strong acid present in very low concentration, the $[In^-]$ terms may be neglected. Determinations of K_e were made for about 30 weak acids and the results shown in Table III.

All determinations were made at at least two different concentrations of acid. Usually, the results were reproducible within 10% and showed no trend with changing concentrations. However, values of K_e below 0.6, where only a small change in optical density resulted from the presence of the acid, were progressively less reproducible. For acids with values of 200 and above, K_e rather consistently increased with decreasing concentration (often increasing 20% as the concentration was halved in the vicinity of 0.01 M).

In order to investigate the influence of a change in solvent,

(13) R. S. Stearns, Ph.D. Thesis, University of Chicago, 1947.

(14) The values of K_e (and K_1) could not be changed to values of $K_i = [H^+][A^-]/[HA]$ since the autoprotolysis constant of isopropyl alcohol does not appear to have been determined.

TABLE III

RELATIVE ACIDITY OF SOME ALCOHOLS AND AMIDES IN ISOPROPYL ALCOHOL SOLUTION

Mannitol and inositol were not sufficiently soluble in isopropyl alcohol to study. A solution of sorbitol gave a precipitate when the sodium isopropoxide was added.

Compound	K_e	Compound	K_e
Isopropyl alcohol	0.076[a]	Phenylacetanilide	10
Benzamide	b	2-Phenoxyethanol	11
N-Methylbenzanilide	b	2-Ethoxyethanol	12
t-Butanol	b	Trimethylene glycol	12
s-Butanol	b	Formamide	13
n-Propanol	ca. 0.5	Tetramethylene glycol	13
i-Butanol	ca. 0.5	Phenoxyacetamide	13
n-Butanol	ca. 0.6	p-Bromobenzamide	15
Ethanol	0.95	Propylene glycol	26
Water	1.20	Ethylene glycol	43
1-Methoxy-2-propanol	1.8	Benzanilide	60
Benzhydrol	2.1	Glycerol	175
Allyl alcohol	2.7	Methyl lactate	210
Benzyl alcohol	3.8	p-Nitrobenzamide	290
Methanol	4.0	p-Bromobenzanilide	380
Acetanilide	5.3	Pentaerythritol	440
2-Aminoethanol	7.7	Formanilide	560
2-Methoxyethanol	8.0	Thioacetamide	ca. 4000

[a] This value is fixed by the definition of K_e. [b] These acids were too weak to measure, probably less than 0.2.

the effect of adding hexane, a poor ion-solvating compound and acetonitrile, the non-acidic solvent with the highest dielectric constant of those available, was studied. At concentrations of 0.03 M, neither had any significant effect on the optical density of an isopropyl alcohol solution of 4-nitrodiphenylamine and sodium isopropoxide of the strengths used in the acidity determinations. At higher concentrations (ca. 0.1 M) the hexane caused a slight but definite decrease in the optical density while the acetonitrile caused a similar increase. It seems likely that since the hydroxylic compounds studied resemble isopropyl alcohol more than hexane and acetonitrile do, their solvent effects should be smaller. As evidence for this, alcohols which would not be expected to be appreciably more acidic than isopropyl alcohol (s- and t-butanol) had no detectable solvent effect even at concentrations of 0.2 M. If the weak acids studied had solvent effects of the same magnitude as hexane and acetonitrile, the resultant error in K_e would be largest where these values are smallest, reaching about 100% at values around 0.5. At K_e values around 2.0, this possible error is about 40%, and it rapidly becomes smaller with higher values of K_e. From Table III it may be seen that methanol was found to be definitely more acidic than water. It might be suggested that water is actually more acidic than methanol, but that its greater acidity is masked by a solvent effect in the same direction as, but considerably larger than, that of acetonitrile. However, this does not seem likely in view of the fact (shown in Table IV) that there was no change (within the limits of experimental error) in the value of K_e for either water or methanol determined at eleven different concentrations, ranging from 0.02

TABLE IV

EFFECT OF CONCENTRATION ON THE VALUES OF K_e FOR WATER AND METHANOL

Water		Methanol	
Concn. M	K_e	Concn., M	K_e
0.0202	1.19	0.0198	3.70
.0407	1.29	.0398	4.06
.0628	1.07	.0627	3.81
.0818	1.24	.0800	3.95
.1024	1.10	.1004	3.92
.1263	1.14	.1263	4.15
.1508	1.13	.1483	4.03
.1804	1.28	.1774	3.84
.2060	1.25	.2019	4.06
.2540	1.25	.2540	4.05
.3032	1.25	.2982	4.09
Av.	1.20 ± 0.07	Av.	3.97 ± 0.11

to 0.30 M (a concentration three times that of the largest used for any of the other acids).

Discussion

Acidity and Basicity of Water and its Alkyl Derivatives.—That the replacement of the hydrogen atom of the hydroxide ion by a methyl group should cause a decrease in basicity should not, perhaps, be surprising in view of the good evidence that the corresponding transformation of water to methanol also produces a decrease (probably larger) in basicity. This decrease is sufficient to make the basicity of water measurable in methanol solution. For the equilibrium constant

$$K = \frac{[MeOH_2^+][H_2O]}{[MeOH][H_3O^+]}$$

values around 0.01 have been obtained, with even lower values found for ethanol.[15] Hammett[16] has based an argument that ethanol is more basic than water on some ionization constants determined by Deyrup.[17] Other determinations differing from those of Deyrup, and analogous data on other compounds[18] would lead to the conclusion that ethanol (and also methanol) is a weaker base than water. Kolthoff, using a somewhat different argument, concluded that water is about 400 times as strong a base as ethanol.[19]

The discovery that the replacement of a hydrogen by an alkyl group may cause a decrease in the basicity of the adjacent atom is not new, of course. It is, on the contrary, well known to be the regular relationship between secondary and tertiary amines. A modification of the "B-strain" hypothesis advanced by Brown and co-workers[20] to explain these data may also be used in explaining the relative basicities of hydroxide and alkoxide anions and of water, alcohols and ethers. Because of the much greater stability when the unshared electrons are in s orbitals, it is believed that the bond angles in R_2O and R_3O^+ (R is any univalent group) would be close to ninety degrees (due to the formation of p bonds) except for steric and dipolar repulsions between the R groups.[21] Both the steric and dipolar effects should be greater with an oxygen compound than with the nitrogen analog to which the same number of groups is attached, since the covalent bond radius of oxygen is smaller and the electronegativity is greater[22] than that of nitrogen.

Since both steric and dipolar repulsions should in-

(15) H. Goldschmidt and O. Udby, Z. physik. Chem., 60, 728 (1907); H. Goldschmidt and A. Thuesen, ibid., 81, 30 (1912); H. Goldschmidt, ibid., 89, 129 (1914); H. Goldschmidt and P. Dahll, ibid., 108, 121 (1924); L. Thomas and E. Marum, ibid., 143, 191 (1929).

(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 260–261.

(17) A. J. Deyrup, THIS JOURNAL, 56, 60 (1934).

(18) H. Goldschmidt, Z. physik. Chem., 99, 116 (1921); H. Goldschmidt and F. Aas, ibid., 112, 423 (1924); H. Goldschmidt and E. Mathiesen, ibid., 119, 439 (1926); L. D. Goodhue and R. M. Hixon, THIS JOURNAL, 56, 1329 (1934); 1. M. Kolthoff and L. S. Guss, ibid., 60, 2516 (1938).

(19) 1. M. Kolthoff, J. Phys. Chem., 35, 2732 (1931).

(20) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, 66, 435 (1944), and many subsequent articles in this series.

(21) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1945, p. 78.

(22) This, of course, would increase the dipolar effect only if the groups attached are, like C and H, less electronegative than the mean of nitrogen and oxygen.
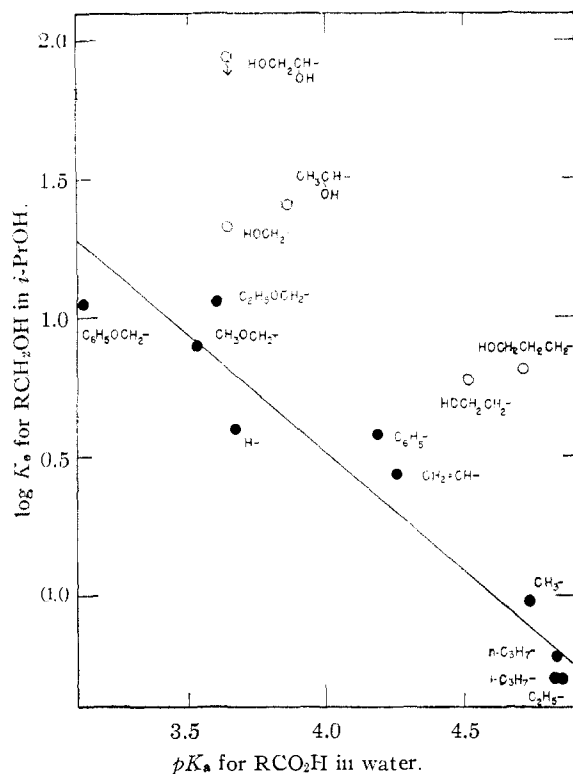
Fig. 2.—Relative effect of various R's on acidity of car-
boxylic acids and primary alcohols: O, glycols; ●, other
alcohols; ⦶, the actual value is an unknown distance be-
low this point.

Fig. 3.—Relative effect of various R's on acidity of car-
boxylic acids and other functional groups: O, methyl-
carbinols; ●, carboxamides; ◑, carboxanilides; ⦶, the
actual value is an unknown distance below this point; *,
value of pK_a estimated from data on related compounds.

crease, it is to be expected that the bond angles
should increase as alkyl groups are progressively
substituted for hydrogen. Oxygen bond angles
observed are: 104°31′ in water,[23] 110°15′ in meth-
anol[24] and 115°50′ in dimethyl ether.[25] The re-
pulsion should be even greater when these oxygen
compounds are protonated because of the greater
number of groups attached to each oxygen and the
increased magnitude of the partial positive charge
on each group.[26] The added strain produced by
transformation into the oxonium ion would be ex-
pected to be greatest when the original molecule
was the most strained. Hence, in opposition to the
effect produced by the electron-donating nature of
alkyl groups, "B-strain" should favor a decrease in
basicity on going from water to alcohols to ethers.
From the data cited on water and alcohols, it ap-
pears that of the two effects, "B-strain" is larger.
The fact that Lemaire and Lucas[27] found that di-n-
butyl ether is too weak a base to measure in acetic
acid solution and is therefore more than one hun-
dred times as weak as water, while dioxane, whose
C–O–C bond angle is held down to about 109°[28] by
a six-membered ring, is sufficiently basic to measure
(about one-fortieth as strong as water) also sup-

ports the "B-strain" hypothesis. In comparing
the effect of "B-strain" on R_2O compounds and
amines, it should be remembered that the increased
bond angles in R_3O^+ compounds signify added
strain, while with the nitrogen compound, the bond
angles of the ammonium ions are much closer to
their preferred 109°28′ than the amines are to
their 90°. From similar considerations it may be
predicted that "B-strain" could decrease the basic-
ity of alkoxide ions as compared to hydroxide ions.
Since this strain is smaller when two groups are at-
tached to oxygen than when three are, it is not sur-
prising that in ethanol, isopropyl alcohol and t-
butanol, where the hyperconjugative resonance is

$$H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\overset{..}{\underset{..}{O}}-H \longleftrightarrow H\overset{\oplus}{\underset{|}{C}}=C\overset{|}{\underset{|}{\overset{\ominus}{O}}}-H$$

increasingly important in the alcohol but made rela-
tively insignificant in the anion, the strain is not
sufficient to reduce the basicity of the related
alkoxide ions below that of the hydroxide ion.
However, it appears that with methoxide the basic-
ity is reduced enough to make methanol a stronger
acid than water. Stabilization of the methoxide
ion by resonance of the type

$$H-\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{\ominus}{\underset{}{O}} \longleftrightarrow H-\overset{H^\ominus}{\underset{H}{\overset{|}{C}}}=O$$

may also be important. The fact that the change
in electronic effect in the series, Me, Et, i-Pr, t-Bu,

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(26) Y. Kakiuchi, H. Shono, H. Komatsu and K. Kigoshi, *J. Chem. Phys.*, **19**, 1069 (1951), estimated the bond angles in the unsubstituted oxonium ion to be about 110°.
(27) H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).
(28) L. E. Sutton and L. O. Brockway, *ibid.*, **57**, 473 (1935); O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947).
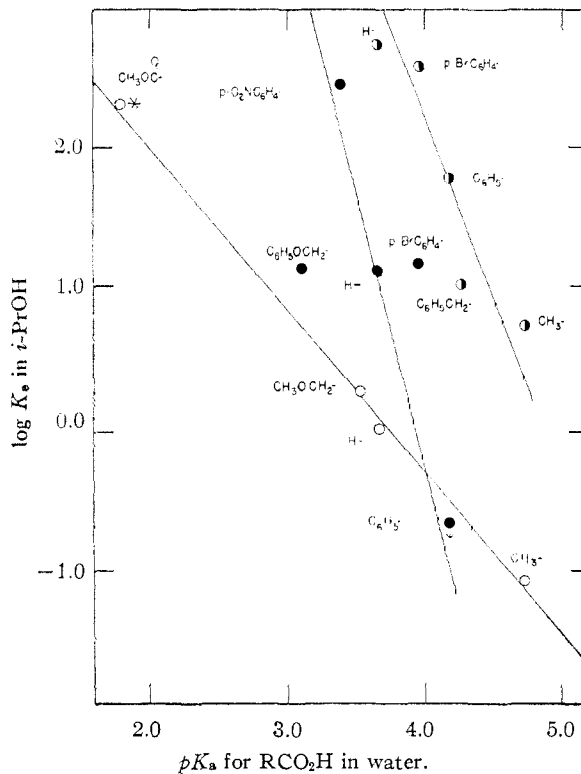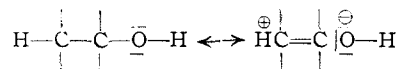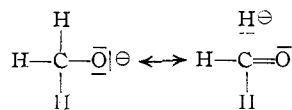
causes a significant increase in basicity of alkoxide anions but appears to have little effect on the basicity of amines may also suggest that there is an opposing effect of "B-strain" which would be more important in the latter equilibrium between tri-valent and tetravalent nitrogen than in the former, between univalent and divalent oxygen.

The Relative Effect of Various "R"'s on the Acidity of Different Functional Groups.—This effect was studied by plotting values of log K (in water)[29] for various RCO_2H compounds against the values of log K_e for the corresponding RCH_2OH, $RCHOHCH_3$, ROH, $RCONH_2$ and $RCONHC_6H_5$ compounds. The values of K_e have been suitably corrected. For example, they have been divided by two in the case of symmetrical glycols. In Fig. 2, the RCH_2OH plot, the data for the hydroxyl-containing R groups have been ignored in drawing the best line, since it seems likely that the anions of the glycols are stabilized by internal hydrogen bonding and hence that the equilibria measured here are really not of the same type as with the monohydroxy alcohols. It is seen that there is a close relation between the effect of an R group on the acidity of $-CO_2H$ and on $-CH_2OH$, but that it is not a perfect one. With the $-CHOHCH_3$, $-CONH_2$ and $-CONHC_6H_5$ compounds plotted in Fig. 3, the situation appears to be similar, but here the number of compounds studied is more limited. The ROH plot displayed very little correlation and is not shown.

(29) Better correlations may have been obtained by using the ionization constants in isopropyl alcohol solution, but these were not available.

Effect of Solvent Changes on Relative Acidity.— All values of K_e are, of course, larger in isopropyl alcohol than in ethanol, but it is interesting to relate the size of the change to the area over which the negative charge is spread in the anion derived from the various acids. From the data in Table V

Compound	K_e in i-PrOH	K_e in EtOH	$\frac{K_e(i\text{-PrOH})}{K_e(\text{EtOH})}$
4,4'-Dinitrodiphenylamine	21600	43.4	500
2,4-Dinitrodiphenylamine	19600	26.68[a]	730
2,4-Dinitroaniline	2700	4.773[a]	570
Ethanol	0.95	0.058	16
Glycerol	175	5.5[a]	32
4-Nitrobenzamide	290	1.4[a]	210

[a] From the data of Stearns and Wheland.[11]

it is seen that this change is smallest with ethanol, where the negative charge is presumably almost entirely on one oxygen atom. It is somewhat larger with glycerol, perhaps indicating that the charge is somewhat dispersed by the hydrogen bonding of an unreacted hydroxyl group to the alkoxide oxygen atom. The largest changes are found with compounds in which the charge may be spread over several atoms by resonance. These data would be expected from the greater ability of ethanol to solvate the anions with more concentrated charges, which are susceptible to stronger solvation.

ATLANTA, GEORGIA

The Freezing Point Curves of Concentrated Aqueous Sulfuric Acid[1]

BY J. E. KUNZLER AND W. F. GIAUQUE

The freezing point composition curves for aqueous sulfuric acid have been investigated over the range $H_2SO_4\cdot2H_2O$–$H_2SO_4\cdot H_2O$ eutectic to somewhat on the SO_3 side of H_2SO_4. The regions near the melting points of H_2SO_4 and $H_2SO_4\cdot H_2O$ have been considered in detail so that the measurements can be used for calculating the change of free energy with composition. Evidence has been presented to show that maximum freezing sulfuric acid corresponds to absolute sulfuric acid within a few thousandths of a wt. %. On this basis we believe that maximum freezing sulfuric acid is a more accurate standard of acidimetry than can be prepared by any other known method. It has been shown that the relative compositions of maximum freezing anhydrous sulfuric acid and the maximum freezing monohydrate correspond to the theoretical H_2SO_4:$H_2SO_4\cdot H_2O$ ratio to within 0.01 wt. % H_2SO_4. Thus maximum freezing $H_2SO_4\cdot H_2O$ is a pure compound within 0.01 wt. % H_2SO_4. The melting points of H_2SO_4 and $H_2SO_4\cdot H_2O$ were found to be 10.371 and 8.489°, respectively.

Work in progress in this Laboratory on the thermodynamic properties of sulfuric acid requires the free energy of dilution. This can be determined from the freezing point curves of the several hydrates. Gable, Betz and Maron[2] have recently published an excellent phase equilibrium diagram of the sulfur trioxide–water system. However, these authors did not contemplate the use of their data for the determination of free energy from the freezing point lowering. A calculation of this type requires numerous precise values near to the

(1) This work was supported in part by the Office of Naval Research, United States Navy.

(2) C. M. Gable, H. F. Betz and S. H. Maron, THIS JOURNAL, **72**, 1445 (1950).

melting points of the several pure phases. It was found desirable to supplement the data of G., B. and M. by very numerous measurements near the melting points of the anhydrous acid and the monohydrate. At the same time measurements of increased accuracy were obtained over the range from the $H_2SO_4\cdot2H_2O$–$H_2SO_4\cdot H_2O$ eutectic to somewhat on the SO_3 side of the anhydrous acid.

Apparatus.—The measurements were made in a one-liter dewar which had a long narrow neck. It was submerged, except for about 2 in. of the neck, in a one-gallon dewar of crushed ice. The sample dewar was equipped with a motor driven stirrer and the tops of both dewars were protected by Bakelite covers. Several small openings, with removable glass sleeves, were provided for the stirrer shaft, sampling, adding increments of the solution components, and for a ten-