The oxygens O_2 and O_5 are coördinated to other sodium ions (O_1 and O_3 take no part in the coördination).

The structure is notable for the large number of close intra- and intermolecular contacts (<3.6 Å.) between oxygens. There are two intermolecular hydrogen bonds (O_1, O_6 and O_3, O_5) and one within the molecule (O_1, O_7).

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RECEIVED MARCH 2, 1960

REGARDING THE SOLVATION OF AMMONIUM IONS AND THE ACIDITY FUNCTIONS, H_R AND H_O[1]

Sir:

The effects on acidity of solvation of ammonium ions and hydronium ion by hydrogen bond formation[2] and the use of the acidity functions, H_O and H_R, as criteria of mechanism[3] are subjects of much current interest. Evidence is herein reported of a close connection between these hitherto unrelated topics.

The acidity functions H_R and H_O are defined as[3]: $H_R = pK_{R^+} - \log (R^+)/(ROH) = -\log a_{H^+} + \log a_{H_2O} + \log (f_{R^+}/f_{ROH})$; $H_O = pK_{BH^+} - \log (BH^+)/(B) = -\log a_{H^+} - \log (f_B/f_{BH^+})$.

The two functions have been found to differ markedly even in dilute acid solutions. For example, in 10–60% sulfuric acid dH_R is roughly twice dH_O.[4] It is apparent from the above definitions that the difference, $H_R - H_O$, must be accounted for in terms of the effect of solvent acidity on the concentration quotient for such equilibria as (in which a term in a_{H^+} is conspicuous by its absence): $BH^+ + ROH \rightleftarrows R^+ + H_2O + B$.

Prompted by the apparent wide applicability of the H_O function, previous suggestions as to the cause of the strong dependence of the above equilibrium on solvent acidity have centered upon the activity coefficient behavior of R^+. Early impressions that unique activity coefficient behavior of R^+ results from the extensive delocalization of charge in aryl methyl cations recently have been dispelled by the demonstration that the NO^+ ion shows virtually equivalent activity coefficient behavior.[3a]

Based upon the evidence which follows, it appears that the R^+ species solvates in a manner conventional to non-hydrogen bond forming cations. "Abnormal" (*i.e.*, additional) interactions are apparently generally involved with BH^+ species. These are hydrogen bonding interactions of the type $B\text{-}H^+ \ldots OH_2$.[2,5] It has been estimated that for equal polar effects of substituent groups on nitrogen, this hydrogen bonding interaction is responsible for a decrease in base strength in aqueous solution of a tertiary relative to a primary amine of about 3.6 powers of ten.[5a] In certain non-aqueous solvents tertiary alkyl amines, as expected by electronic arguments, are actually more basic than primary amines.[6]

In the region 44–64% H_2SO_4, a very simple correlation exists between ($H_R - H_O$) and the activity of water, *cf.* Fig. 1. Seven arylmethanols were used to establish the H_R function in this region and within experimental error no dependence of H_R on structure can be noted.[4] On the other hand, two amines were used to establish the H_O function, *p*-nitrodiphenylamine and 2,4-dichloro-6-nitroaniline.[7] Close inspection of the original data reveals a measurable difference in H_O for these two indicators. The difference is illustrated in Fig. 1, which shows a closely linear relationship between ($H_R - H_O$) and $\log a_{H_2O}$ of slope 4 with H_O based upon the latter amine and a similar relationship of slope 3 with H_O based upon the former amine.

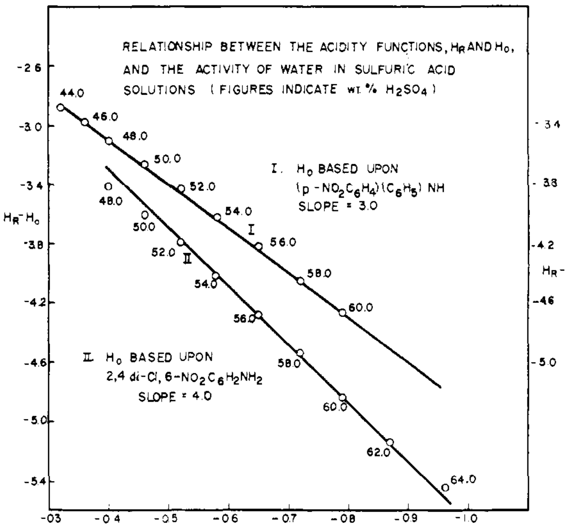
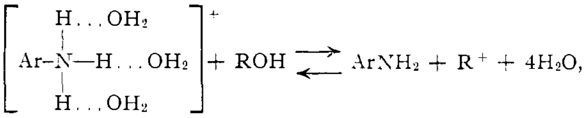


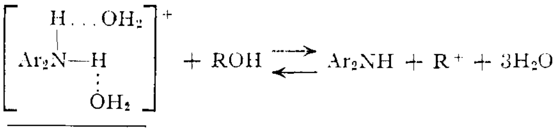
Fig. 1.

The particular values of the integral slopes of Fig. 1 are strongly suggestive that these equilibria are effectively operative



$$\left[\begin{array}{c} H\ldots OH_2 \\ | \\ Ar\text{-}N\text{—}H\ldots OH_2 \\ | \\ H\ldots OH_2 \end{array}\right]^+ + ROH \rightleftarrows ArNH_2 + R^+ + 4H_2O,$$

and



$$\left[\begin{array}{c} H\ldots OH_2 \\ | \\ Ar_2N\text{—}H \\ \vdots \\ OH_2 \end{array}\right]^+ + ROH \rightleftarrows Ar_2NH + R^+ + 3H_2O$$

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[1] This work was supported in part by the Office of Naval Research.

[2] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chap. IV, V and VI, and references given therein.

[3] (a) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, THIS JOURNAL, **81**, 2344 (1959); (b) J. F. Bunnett, *ibid.*, **82**, 499 (1960); (c) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *ibid.*, **82**, in press (1960); (d) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

[4] N. C. Deno, J. J. Jaruzelski and A. Schriesheim THIS JOURNAL, **77**, 3044 (1955).

[5] (a) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); (b H. K. Hall, Jr., THIS JOURNAL, **79**, 5441 (1957).

[6] R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958).

[7] L. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).

and that $[f_{BH_n^+\cdot(H_2O)_n}f_{ROH}]/f_{R^+}f_B \cong 1$ (in addition since there is evidence that $f_{ROH}/f_B = 1$ for this region of acidity,[3a,8] $f_{BH_n^+\cdot(H_2O)_n} \cong f_{R^+}$).

In the region 60–75% H_2SO_4, H_O was obtained[7] for two primary amines, 2,6-dinitro-4-methylaniline and 2,4-dinitroaniline, of closely similar behavior and a tertiary amine, N,N-dimethyl-2,4,6-trinitroaniline, whose behavior has been recognized as "divergent."[8] These results are illustrated in Fig. 2 in which again ($H_R - H_O$) is plotted *vs.* log a_{H_2O}.

The plots of Fig. 2 lead to curved rather than linear relationships. However, this result is perhaps expected in terms of the above interpretation in view of the limited availability of "excess" water molecules for hydrogen bonding with the anilinium ions. It appears significant that the curve for the tertiary amine rapidly approaches an approximately unit slope, whereas the slope for the primary amines is distinctly greater than unity throughout this region of acidity. The former behavior is consistent with earlier evidence suggesting that the single proton of the conjugate acid of a *tert.* amine is relatively poorly solvated by hydrogen bonding.[5b] It is well known[8] that in the region of no excess water molecules (83–100% sulfuric acid) H_R differs quite generally from H_O by log a_{H_2O}.

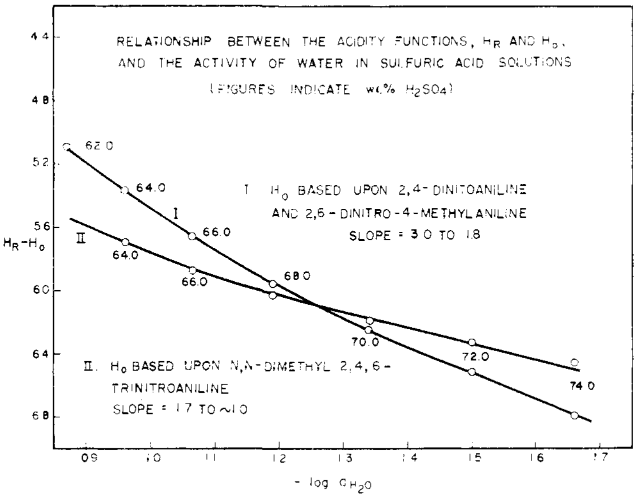

Fig. 2.

Similar plots of ($H_R - H_O$) *vs.* log a_{H_2O} in the acidity region below 40% H_2SO_4 are curved with slopes distinctly larger than 3 or 4. These results suggest that with an abundance of available water molecules, additional hydrogen bonding (and perhaps other 3a) interactions of weak and variable strengths occur (with $BH^+_n\cdot(H_2O)_n$, ROH, and B) thus invalidating the activity coefficient relationship proposed above.

The present proposals have important consequences concerning acidity function theory and prompt additional investigation and review of previously accepted concepts. It is of interest to note that Bell's recent interpretation (along rather similar lines) of the H_O function in terms of the $H_9O_4^+$ ion, apparently imposes the conditions:[2] $f_{ArNH_3^+}/f_{H_9O_4^+} \cong 1$. In terms of the present evidence, it appears that the $H_9O_4^+$ ion ($H_3O^+\cdot(H_2O)_3$), must be further solvated to a weaker extent by hydrogen bonding interactions of similar strength and degree to those involved with the $ArNH_3^+$ ions.

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[8] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

SYNTHESIS OF VANADIUM HEXACARBONYL

Sir:

Some properties and the structure of the vanadium hexacarbonyl have been described.[1] The existence of this compound demonstrates, for the first time, that a transitional element with atomic number lower than 24 is able to form a true carbonyl. Here we describe the synthesis of the $V(CO)_6$ as well as the preparation of salts of $[V(CO)_6]^-$ anion.

Simple and easily available vanadium compounds such as anhydrous VCl_3, $VOCl_3$, V(III) acetylacetonate are caused to react at 80–150° with a metal–amine reducing system and with pressurized carbon monoxide. Using Mg + Zn and excess of pyridine as reducing agent, the carbonylation of vanadium compounds occurs easily at 120–140° with consumption of about the theoretical amount of carbon monoxide. This method for the "reducing carbonylation" of transitional elements was reported previously[2] for a high yield synthesis of $Cr(CO)_6$ and was proved to be operative also to prepare other metal carbonyls, especially $Mo(CO)_6$. It is noteworthy that the carbonylation of vanadium compounds does not afford free $V(CO)_6$ directly as it normally occurs in the $Cr(CO)_6$ synthesis. Actually the reduction of vanadium goes further, the metal being present in the carbonylation products principally in the −1 state as $[V(CO)_6]^-$. In fact, working up the reaction mixture, aqueous solutions can be obtained from which the salts: $Ni(o\text{-fen})_3[V(CO)_6]_2$ as well as Na.2 dioxane $[V(CO)_6]$ can be isolated. Moreover the vanadium hexacarbonyl is obtained in fairly good yields (40–50%) when the residue from evaporating the liquid phase of the reaction mixture is acidified and ether extracted. An evidence for an intermediate hydrocarbonyl lies in the rapid evolution of hydrogen observed during the concentration of the ethereal layer.

Thus the carbonylation products are suitable for preparing either the $V(CO)_6$ or the salts of the anion $[V(CO)_6]^-$. The latter also can be obtained by the reaction of the hexacarbonyl with Lewis bases such as di-*n*-butyl ether, dioxane, pyridine, methanol, acetone, according to the scheme

$$3V(CO)_6 + nB \longrightarrow V(B)_n[V(CO)_6]_2 + 6CO$$

The vanadium hexacarbonyl is a volatile, air sensitive, blue-green substance which decomposes at 60–70° (capillary sealed under N_2). In the solid state, it is paramagnetic for 1 electron and has a crystal

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[1] G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini and G. Allegra, *Rend. Accad. Naz. Lincei*, [8] **27**, 107 (1959).

[2] G. Natta, R. Ercoli, F. Calderazzo and A. Rabizzoni, THIS JOURNAL, **79**, 3611 (1957); R. Ercoli, F. Calderazzo, G. Bernardi, *Gazz. Chim.*, **89**, 809 (1959).