

Fig. 2.

favor recombination of the "hot" Cr with radicals produced by radiation damage, in spite of their low concentration relative to water molecules. The extent of the radiation-induced decomposition can be seen from the distribution of the total Cr, initially present as $\text{Cr}(\text{NCS})_6^{3-}$. Extensive conversion to $\text{Cr}(\text{NCS})_5(\text{H}_2\text{O})^{-2}$ occurred, but the amount of lower complexes formed is relatively small.

The ratio of *trans*- to *cis*- $\text{Cr}(\text{NCS})_2(\text{H}_2\text{O})_4^+$ is 0.31 for both the radioactivity and the total Cr, as compared to the equilibrium value³ of 0.5 at 370°K. About 11% of the radioactivity fell outside of the main peaks, and two small unidentified peaks can be seen in the cation elution curve. These may be due to complexes with fragments of the NCS^- group, such as $\text{Cr}(\text{NC})(\text{H}_2\text{O})_5^{+2}$ or $\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{+3}$.

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THE STATE OF IONIZATION OF CRYSTALLINE SODIUM DIHYDROGEN CITRATE¹

Sir:

The structure of sodium dihydrogen citrate has been determined by three-dimensional X-ray diffraction methods. This substance crystallizes in

(1) Supported by a grant (C1253) from the National Cancer Institute, Public Health Service.

the monoclinic space group $P2_1/a$ with 4 molecules of $\text{NaH}_2(\text{C}_6\text{O}_7\text{H}_5)$ in a cell of dimensions $a = 9.648 \text{ \AA}$, $b = 11.680 \text{ \AA}$, $c = 7.481 \text{ \AA}$, $\beta = 105^\circ 15'$. The observed density was $1.747 \text{ g. cm.}^{-3}$ while that calculated was $1.749 \text{ g. cm.}^{-3}$. The standard error in axial lengths is less than $\pm 0.13\%$ and in angle less than $\pm 6'$. The observed density was reproducible to 1%.

The analysis was based on 1917 independent reflections photographed with $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation. Of these 223 were too weak to be measured. The trial structure was found from a three-dimensional sharpened F^2 -map and refined by two- and three-dimensional difference Fourier series and by three-dimensional least-squares methods with individual isotropic temperature factors.² At the present stage of refinement the reliability factor R is 13.2% for all reflections. All seven hydrogen atoms have been located on a difference synthesis.

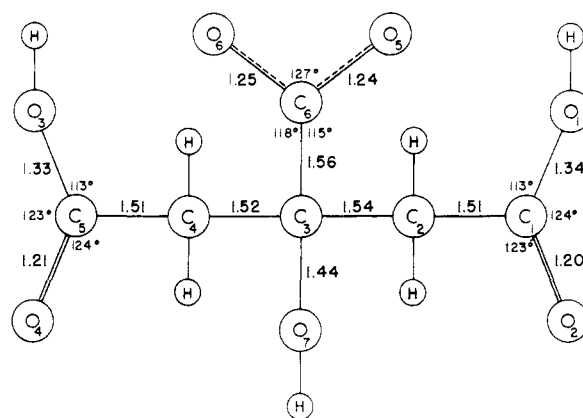


Fig. 1.

The covalent bond lengths and angles in the citrate ion are shown in the diagram. Of the three carboxyl groups, the two end carboxyls have C—O distances which are non-equivalent (1.20, 1.34 and 1.21, 1.33 Å.) whereas the central carboxyl has two equivalent C—O distances (1.24, 1.25 Å.). The bond angles confirm these relations. These findings together with the observed attachment of hydrogen atoms to O_1 and O_3 demonstrate that it is the central carboxyl group which is ionized in this crystal. It is interesting to note that nuclear magnetic resonance measurements³ indicate that in solution the singly ionized citrate is predominately ionized in the end carboxyl groups.

Although full discussion of the structure will be reported elsewhere it is worth while noting that the sodium ion is octahedrally coordinated to oxygens. These octahedra occur in centrosymmetrically related pairs with one edge shared ($\text{O}_7\text{O}_7'$). Each molecule forms two bidentate chelate rings, one with each of the sodium ions of the above-mentioned pairs of octahedra. One of the chelate rings is five-membered ($\text{NaO}_6\text{C}_6\text{C}_5\text{O}_7$) and the other is six-membered ($\text{Na}'\text{O}_4\text{C}_6\text{C}_4\text{C}_3\text{O}_7$).

(2) We are indebted to Princeton University and to Indiana University for the use of their computation facilities.

(3) A. Loewenstein and J. D. Roberts, *THIS JOURNAL*, **82**, 2765 (1960).

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

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

(4) Jenkins Laboratory of Biophysics, The Johns Hopkins University, Baltimore, Maryland.

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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 formation² and the use of the acidity functions, H_O and H_R , as criteria of mechanism³ 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 as³: $H_R = pK_{R^+} - \log (R^+)/(\text{ROH}) = -\log a_{H^+} + \log a_{H_2O} + \log (f_{R^+}/f_{\text{ROH}})$; $H_O = pK_{\text{BH}^+} - \log (\text{BH}^+)/(\text{B}) = -\log a_{H^+} - \log (f_{\text{B}}/f_{\text{BH}^+})$.

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): $\text{BH}^+ + \text{ROH} \rightleftharpoons \text{R}^+ + \text{H}_2\text{O} + \text{B}$.

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.^{5a}

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.

(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).

These are hydrogen bonding interactions of the type $\text{B-H}^+ \dots \text{OH}_2$.^{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

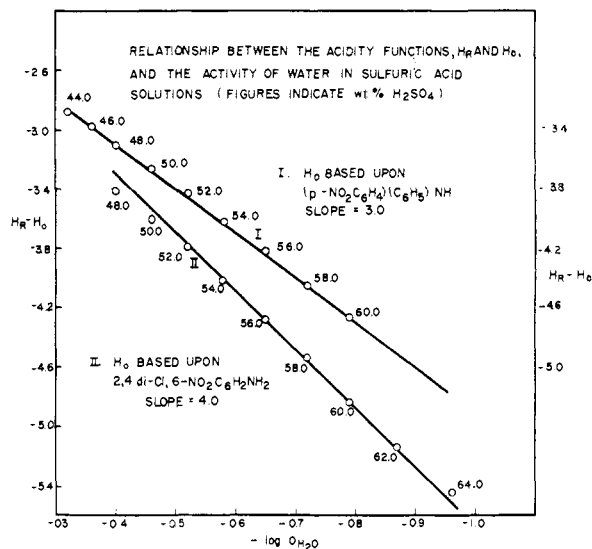
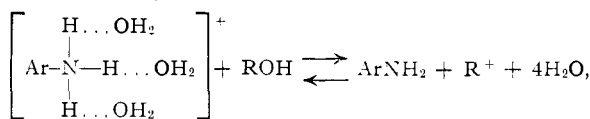


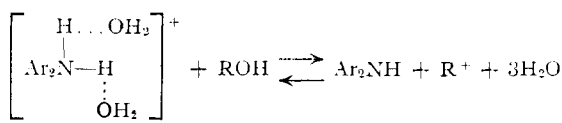
Fig. 1.

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 $\log a_{\text{H}_2\text{O}}$ 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.

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



and



(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) I. P. Hammett and A. J. Deyrup, *ibid.*, **54**, 2721 (1932).