

shows the  $\nu$ , for free OH at 3630  $\text{cm}^{-1}$  and a new band at 3483  $\text{cm}^{-1}$  but no band at 3330  $\text{cm}^{-1}$ . This is in contrast with a solution of alcohol alone in carbon tetrachloride: free OH band at 3634  $\text{cm}^{-1}$  and alcohol-alcohol bonded OH band at 3330  $\text{cm}^{-1}$ . The 3483  $\text{cm}^{-1}$  band is not present in the absence of benzyl isocyanide nor is it present in the benzyl isocyanide spectrum in the absence of alcohol. The intensity of this new band grows with increasing benzyl isocyanide concentration, at constant alcohol concentration, at the expense of the free OH band. Furthermore, in dilute solutions of alcohol in benzyl isocyanide as solvent, the intensity of the 3483  $\text{cm}^{-1}$  band is proportional to alcohol concentration and the free OH band is very small if not absent. The position of the new band and its direct relationship to isocyanide and alcohol concentrations constitute proof of a hydrogen bond between these two molecules.

The hydrogen bond is, almost without a doubt, to the carbon in the isocyanide group. The most compelling evidence for this is that this carbon is the most negative site in the molecule. According to

Pauling, the canonical form  $\text{CH}_3\text{N}^+\equiv\text{C}^-$ : contributes 74% to the resonance hybrid of methyl isocyanide.<sup>5</sup> In benzyl isocyanide, this sort of polarized form should contribute even more to the hybrid. Therefore, the electron seeking hydrogen should bond to carbon rather than electron deficient nitrogen. Other possible sites for the hydrogen bond are with the  $\pi$  electrons in the ring or in the N to C bond. The ring  $\pi$  electrons, which form only weak hydrogen bonds at best,<sup>1</sup> would be no better and perhaps even poorer as a site for hydrogen bonds in benzyl isocyanide than in alkylaromatic compounds. Furthermore, the shift in  $\nu$ , for hydrogen bonds to aromatic systems is never as large<sup>1</sup> as shown in this case. The  $\pi$  electrons of the N to C bond probably are even weaker hydrogen bonding sites than either the aromatic  $\pi$  electrons or acetylene  $\pi$  electrons which are also very weak.<sup>1</sup>

The strongly basic carbon in isocyanides will form a *carbon-hydrogen-carbon bond* with certain compounds. Phenylacetylene has been reported to be a hydrogen donor with several conventional bases.<sup>6</sup> In this work, infrared evidence for a hydrogen bond between benzyl isocyanide and phenylacetylene was found to be similar to that for phenylacetylene and benzonitrile, a conventional base. The acetylenic C-H stretching band shifts about 30  $\text{cm}^{-1}$  to lower wave numbers in benzyl isocyanides as solvent. While it is a small shift, it is almost identical with the shift in benzonitrile as base. More impressive evidence for the acetylenic hydrogen bond is found in dilute solutions of the acetylene and benzyl isocyanide in carbon tetrachloride. Under these conditions, the original C-H band at 3314  $\text{cm}^{-1}$  is present as well as a shoulder about 30  $\text{cm}^{-1}$  lower. This phenomenon is best explained by a mixture of bonded C-H and free C-H. A single but shifted band would be

expected by a mere change in the dielectric constant of the medium.

Thus, isocyanides form hydrogen bonds with typical hydrogen donors. These bonds are strong; it appears that the benzyl isocyanide-alcohol bond is even stronger than the benzonitrile-alcohol bond. Details of the above data and a comparison of the strength of these bonds and other hydrogen bonds will be published soon.

CALIFORNIA RESEARCH CORPORATION  
RICHMOND, CALIFORNIA

LOUIS L. FERSTANDIG

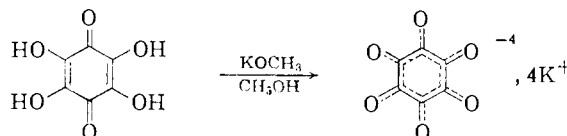
RECEIVED NOVEMBER 9, 1961

SYMMETRICAL RESONANCE STABILIZED ANIONS,  $\text{C}_n\text{O}_n^{-m}$ . II.  $\text{K}_4\text{C}_6\text{O}_6$  AND EVIDENCE FOR  $\text{C}_6\text{O}_6^{-3}$

Sir:

In an earlier communication<sup>1</sup> it was pointed out that anions of the type  $\text{C}_n\text{O}_n^{-2}$  represent a previously unrecognized series of symmetrical aromatic anions. It now appears that this series can be generalized to include anions of other charge types. In particular, we now wish to report isolation of the tetrapotassium salt of the anion  $\text{C}_6\text{O}_6^{-4}$ , and evidence for the possible existence of the radical-anion  $\text{C}_6\text{O}_6^{-3}$ .

The anion  $\text{C}_6\text{O}_6^{-4}$  is obtained directly from tetrahydroxyquinone (THQ) by removal of four protons:



However, special technique is necessary to avoid the precipitation of the insoluble dipotassium salt of THQ, and scrupulous care must be taken to prevent oxidation of the anion. All of the operations must be carried out in an inert atmosphere. In a typical run a solution of 30 mg. of THQ in 10 ml. of dry oxygen-free methanol was slowly injected into a solution of 5 g. of potassium metal in similarly pure methanol, at room temperature.  $\text{K}_4\text{C}_6\text{O}_6$  precipitated immediately as a black powder. The methanol solution was drawn off and replaced successively with deoxygenated samples of tetrahydrofuran and ether. After removal of most of the ether, the product was dried *in vacuo*. *Anal.* Calcd. for  $\text{K}_4\text{C}_6\text{O}_6$ : K, 48.2; C, 22.30; H, nil. Found: K, 47.0; C, 22.82; H, nil.

The infrared spectrum of  $\text{K}_4\text{C}_6\text{O}_6$  contains five bands in the 350–4000  $\text{cm}^{-1}$  region. The anion must therefore have a highly symmetric structure, since models with low symmetry would be expected to give many more infrared bands. However, the totally symmetric planar structure ( $D_{6h}$ ) should give rise to only three infrared-active fundamentals in this region. The observed spectrum is compatible with a structure in which the C-C and C-O distances are all equal with the ring slightly puckered into a chair form ( $D_{3d}$  symmetry).<sup>2</sup> In the visible region, solid  $\text{K}_4\text{C}_6\text{O}_6$

(1) R. West, H.-Y. Niu, D. L. Powell and M. V. Evans, *J. Am. Chem. Soc.*, **82**, 6204 (1960), which should be regarded as paper I of this series.

(2) Calculations indicate that the anion could adopt this non-planar puckered form with only a small loss in aromatic resonance energy.<sup>3</sup>

(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, Third Edition, 1960, p. 270.

(6) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961).

exhibits two very broad bands centered at about 5400 and 6700 Å. In water the compound is rapidly oxidized to rhodizonate ion,  $C_6O_6^{-2}$ .

The magnetic properties of  $C_6O_6^{-4}$  are of especial interest in connection with its electronic structure. Simple LCAO molecular orbital calculations<sup>3</sup> predict a biradical nature for  $C_6O_6^{-4}$ . However, measurements by the Gouy method show that  $K_4C_6O_6$  is diamagnetic. The compound may be one in which electron correlation effects, neglected in the simple MO approach, operate to prevent the degeneracy. Similar arguments have been used to predict a non-degenerate ground state for cyclobutadiene.<sup>4</sup> A complete treatment of  $C_6O_6^{-4}$ , including configuration interaction, would present a formidable theoretical problem.

Pure  $K_4C_6O_6$  gives no electron spin resonance signal, but the compound is rapidly oxidized upon

The rhodizonate anion in the crystalline salts  $Na_2C_6O_6$  and  $K_2C_6O_6$  appears also to have a non-planar or otherwise distorted geometrical form.

(3) D. L. Powell, M. Ito and R. West, unpublished work.

(4) D. P. Craig, *Proc. Roy. Soc. (London)*, **A202**, 498 (1950); cf. A. D. Liehr, *Z. physik. Chem., N. F.*, **9**, 338 (1956).

exposure to air, with the development of a strong esr signal. Incomplete oxidation of  $K_4C_6O_6$  under ether also converts it to a strongly paramagnetic solid, green in color, with a single electron spin resonance near  $g = 2.003$ . A similar green salt may be obtained instead of  $K_4C_6O_6$  in the preparation described above if a small amount of oxygen is present. Further oxidation converts the green salt to potassium rhodizonate, but samples stored in the absence of oxygen maintain their radical nature almost undiminished for several months. It has not yet proved feasible to prepare this radical substance in pure form, but observations so far are consistent with the hypothesis that the green salt may contain the tripotassium salt of the aromatic radical-trianion,  $C_6O_6^{-3}$ .

**Acknowledgments.**—The authors are indebted to Dr. Mitsuo Ito and Mr. David Powell for many helpful discussions, and to The National Science Foundation for support of this investigation.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON 6, WISCONSIN

ROBERT WEST  
HSIEN YING NIU

RECEIVED JANUARY 22, 1962

---

## BOOK REVIEWS

---

**Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest.** By H. GOBIND KHORANA, Institute for Enzyme Research, University of Wisconsin. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1961. ix + 141 pp. 15.5 × 23.5 cm. Price, \$5.25.

This volume derives from a series of lectures given at the Rockefeller Institute in 1959, but is up-dated with many references into 1961. It naturally emphasizes the author's interests but is an essential for those interested in nucleotide and polynucleotide syntheses. The first twelve-page chapter is a survey of phosphate compounds of importance in biological reactions and is certainly worthy of attention by any graduate student.

SLOAN-KETTERING DIVISION OF  
CORNELL UNIVERSITY MEDICAL COLLEGE  
NEW YORK 21, N. Y.                      GEORGE BOSWORTH BROWN

**The Electrical Double Layer Around a Spherical Colloid Particle. Computation of the Potential, Charge Density, and Free Energy of the Electrical Double Layer Around a Spherical Colloid Particle.** By A. L. LOEB, Associate Professor of Electrical Engineering, Massachusetts Institute of Technology, J. TH. G. OVERBEEK, Professor of Physical Chemistry, University of Utrecht, and P. H. WIERSEMA, van't Hoff Laboratory, University of Utrecht. The M.I.T. Press, Massachusetts Institute of Technology, Cambridge, Massachusetts. 1961. 375 pp. 18.5 × 26 cm. Price, \$10.00.

This book reports the numerical integration of the Poisson-Boltzmann equation for spherical colloidal particles in electrolytic solution. Results are presented in terms of reduced (*i.e.*, dimensionless) quantities. First,  $y$  (reduced electrostatic potential) is calculated as a function of  $x$  (reduced reciprocal distance from center of particle) with  $y_0$  and  $q_0 = 1/x_0$  ( $x_0$  and  $y_0$  are values of  $x$  and  $y$  at particle surface, outer Helmholtz plane, or slipping plane depending on application) as parameters.  $I_+$  and  $I_-$  ( $x^2/4$  times excess charge due to cation and anion outside of a sphere of reduced radius  $1/x$  centered on the particle center) and

the reduced double layer free energy  $F$  are calculated from the previously calculated dependence of reduced potential on reduced reciprocal distance. Tabular results are given for 1-1, 2-1, 3-1, 1-2 and 1-3 electrolytes; data for other symmetric electrolytes (2-2, 3-3 etc.) can be calculated readily from results for 1-1 electrolytes.

Part I of the book (pp. 1-42) describes the method of integration, including transformations of variables to dimensionless groups, an outline of the numerical integration method selected for IBM-704 computer programming, and an outline of methods for transforming tabular results (all in dimensionless groups) into quantities of physical interest. Results of the present calculation are compared with those of the Debye-Hückel approximate treatment and the flat plate double layer. Empirical analytical forms representing data for  $I$  and  $F$  to within 26% and 20%, respectively, are also given. Part I contains 28 tables.

Part II (pp. 46-372) presents the dependence of  $y$ ,  $I_+$ ,  $I_-$ , and  $F$  on  $x$  with  $y_0$  and  $q_0$  as parameters in tabular form for 1-1, 2-1, 3-1, 1-2 and 1-3 electrolytes. Computations for 1-1 electrolytes are particularly extensive (pp. 46-208); results for  $q_0 = 0.1$ , for example, are presented for the range  $0.3 \leq x \leq 10.0$  in units of 0.1 for  $1 \leq y_0 \leq 16$  with increments of 1 from 1-10, 2 from 10 to 16; this is repeated with reduced ranges of  $x$  for  $q_0 = 0.2, 0.5, 1.0, 2.0, 5.0, 10$  and  $20$ . For values of  $x$  smaller than those tabulated the Debye-Hückel approximation is adequate. The authors state that numerical interpolation between tabulated results will generate results accurate to 0.1% if carefully done; linear interpolation between values of  $x$  for fixed  $q_0$  and  $y_0$  appears generally possible to within 1%, but interpolation between different values of  $q_0$  and  $y_0$  will require more refined interpolation involving, for example, ratios of tabulated quantities to approximate or empirical analytical representations of them.

This is a specialist's book concerned principally with numerical results. These results appear to be carefully obtained, and to reflect solutions of the Poisson-Boltzmann equation of adequate precision and detail covering a wide range of parameters. The authors point out that the Debye-Hückel approximation to the Poisson-Boltzmann equation is only valid if  $Zey/kT \ll 1$ . Applicability of