

concentration. The fact that the NO concentration in the photolysis cell becomes very small indicates simply that NO is being chemically consumed much faster than it leaks out of the photolysis cell into the mass spectrometer. The nitric oxide steady state concentration in the photolysis cell will therefore be proportional to the rate at which it diffuses into the cell from the reactant reservoir. After the CD_3NO maximum the NO concentration in the photolysis cell is very much less than the NO concentration in the reservoir, and therefore, the diffusion rate into the photolysis cell will be approximately proportional to the NO concentration in the reactant reservoir. The result is that, after the CD_3NO maximum, the steady state concentration of NO will be approximately proportional to the initial concentration of NO.

Although we cannot measure quantitatively the NO concentration, after the CD_3NO maximum, the rate of reaction 3 is sufficiently great⁴ that the actual steady state concentration of CD_3 will be influenced by the steady state NO concentration. Thus, because of reaction 3, the actual CD_3 concentration will be a decreasing function of the initial nitric oxide concentration and in all cases will be lower than that calculated by E5; the difference between the actual and the calculated CD_3 concentrations will, of course, diminish as the initial NO concentration is reduced. Since E5 overestimates the steady state CD_3 concentration, the

treatment described underestimates k_4 , with the amount of underestimation decreasing and becoming zero as the initial NO concentration approaches zero. Thus, the values of k_4 in Table II are all lower limits to k_4 and, in principle, the true value could be obtained by extrapolation of k_4 to $[\text{NO}]_0 = 0$. Unfortunately, k_4 is a complicated function of $[\text{NO}]_0$ and our data do not permit a reliable extrapolation to be made. Nonetheless, we can say that $k_4 > 6.51 \times 10^{-14}$ cm.³/molecule sec. and despite the uncertainty in the upper limit it is evident that 4 is a very fast reaction having a collision yield (assuming a collision diameter of 4.0 Å.) at 25° of 1.9×10^{-4} . The specific reaction rate of 4 is sufficiently high that the occurrence of 4 and 5 must be considered in the analysis of free radical reactions inhibited by nitric oxide. These reactions obviously will be of particular importance in nitric oxide inhibited reactions conducted over temperature ranges wherein $(\text{CD}_3)_2\text{NO}$ and $(\text{CD}_3)_2\text{NOCD}_3$ are thermally stable.

Acknowledgment.—We wish to thank Miss Kathleen Muller for her assistance with the calculations. This work was supported in part by the Petroleum Research Fund Grant 833-A1 and in part by contract AF33(616)-7716 with the Office of Aerospace Research. We are also pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Bendix Time-of-Flight mass spectrometer.

[CONTRIBUTION FROM THE PARKINSON LABORATORY OF SOUTHERN ILLINOIS UNIVERSITY, CARBONDALE, ILL.]

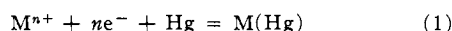
The Influence of Ionic Strength on Polarographic Half-Wave Potentials. I. Aqueous Systems Involving Reversible Electrode Reactions and Amalgamation of the Reduced Species in Uni-univalent Inert Electrolytes

BY DOUGLAS E. SELLERS AND NICHOLAS E. VANDERBORGH

RECEIVED NOVEMBER 6, 1963

A method for the mathematical estimation of the change in the observed half-wave potential of a metal ion with changes in the concentration of the inert (supporting) electrolyte is derived. A method for the correlation of half-wave potentials in systems of high ionic strength and for the correction of polarographically determined dissociation constants (where the ionic strength is maintained constant by varying the concentrations of different ionic species) is implied.

For the polarographic investigation of simple metal ions, the reduction to the metallic state (amalgams) has been represented¹ simply as



where M^{n+} represents the simple, hydrated metal ion. The potential of the dropping electrode, when the reaction is rapid and reversible, is given¹ by

$$E_{d.e.} = E_a^\circ - \frac{RT}{nF} \ln \frac{C_a^0 y_a}{a_{\text{Hg}} C_s^0 y_s} \quad (2)$$

where C_a^0 and C_s^0 are the molar concentrations of the reduced or reducible species in the amalgam and solution at the surface of the drop, respectively; the terms y_a and y_s are the corresponding molar activity coefficients and a_{Hg} is the activity of the mercury. The corresponding representation of the half-wave potential, considering the effect of the liquid junction potential,

has been given² as

$$E_{1/2} = \epsilon - E_L + \frac{RT}{nF} \ln y_s - \frac{RT}{2nF} \ln (D_s/D_a) \quad (3)$$

where D_a and D_s are the diffusion coefficients of the metal in mercury and in solution, respectively; the constant ϵ is equal to $E_a^\circ - RT/nF \ln (y_a/a_{\text{Hg}})$.

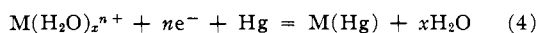
However, if polarographic measurements are to be carried out in aqueous systems of high concentrations of inert electrolyte, a question arises as to the constancy of the activity of water, as is assumed in the statements of eq. 1 and 3, the influence of the high ionic strength on y_s ; the magnitude of the change of E_L ²; the liquid junction potential, as well as other factors.³ It appears doubtful that such simplifying assumptions which are made in the usual derivation of eq. 3 are valid in such instances and has been illustrated by DeFord and Anderson.²

(2) D. D. DeFord and D. L. Anderson, *J. Am. Chem. Soc.*, **72**, 3918 (1950).

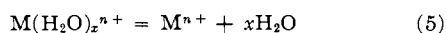
(3) W. B. Schaap, *ibid.*, **82**, 1837 (1960).

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

In view of these considerations, a more representative over-all electrodes process may be



where the hydrated species is in equilibrium with the simple metal ion (or at least a species of lower hydration number) as represented by



(assuming for the present that no complex or ion-pair formation exists between the reducible species and the anion of the inert electrolyte). The concentration of the nonhydrated species at the electrode surface may be represented, by the method of DeFord and Hume,⁴ as

$$C_{M^{n+}}^0 = \frac{C_{M(H_2O)_x^{n+}}^0 y_{M(H_2O)_x^{n+}}}{y_{M^{n+}} (a_w)^x K_H} \quad (6)$$

where $C_{M^{n+}}^0$ and $C_{M(H_2O)_x^{n+}}^0$ are the concentrations of the nonhydrated and hydrated reducible species at the electrode surface, $y_{M^{n+}}$ and $y_{M(H_2O)_x^{n+}}$ are the corresponding molar activity coefficients, a_w is the water activity, and K_H is the hydration constant for the reducible species at ionic strength equal to μ and is defined as

$$K_H = K_1 \cdot K_2 \cdot \dots \cdot K_x$$

where

$$K_1 = \frac{C_{M(H_2O)^n} + y_{M(H_2O)^n}}{C_{M^{n+}} + y_{M^{n+}} + a_w}$$

Thus, the potential at the dropping electrode is

$$(E_{1/2})_\mu = \epsilon - (E_L)_\mu - \frac{RT}{2nF} \ln \frac{D_{M(H_2O)_x^{n+}}}{D_a} + \frac{RT}{nF} \ln y_{M(H_2O)_x^{n+}} - \frac{RT}{nF} \ln K_H (a_w)^x \quad (7)$$

where $(E_{1/2})_\mu$ and $(E_L)_\mu$ are the half-wave and liquid junction potentials expressed as a function of the ionic strength.

As the ionic strength approaches zero, eq. 7 assumes the form

$$(E_{1/2})_{\mu=0} = \epsilon - (E_L)_{\mu=0} - \frac{RT}{2nF} \ln \frac{D_{M(H_2O)_x^{n+}}}{D_a} - \frac{RT}{nF} \ln K_a \quad (8)$$

with $y_{M(H_2O)_x^{n+}} \cong a_w \cong 1$ at polarographic concentrations of the reducible species in which a represents the hydration parameter at ionic strength equal to zero.

The subtraction of eq. 8 from eq. 7 yields

$$(E_{1/2})_\mu - (E_{1/2})_{\mu=0} = (E_L)_{\mu=0} - (E_L)_\mu - \frac{RT}{nF} \left\{ \frac{1}{2} \ln \frac{D_{M(H_2O)_x^{n+}}}{D_{M(H_2O)_x^{n+}}} - \ln y_{M(H_2O)_x^{n+}} + \ln \frac{K_H}{K_a} + x \ln a_w \right\} \quad (9)$$

It has been shown that the hydration parameter, x or a as the case might be from the previous discussion, re-

mains essentially constant over a fairly wide range of ionic strength values.⁵ If the ratios $D_{M(H_2O)_x^{n+}}/D_{M(H_2O)_x^{n+}}$ and K_H/K_a may be considered as unity, than eq. 9 can be reduced to

$$(\Delta E_{1/2})_{\text{obsd}} = \frac{RT}{nF} \left\{ \ln y_{M(H_2O)_x^{n+}} - x \ln a_w \right\} \quad (10)$$

with

$$(\Delta E_{1/2})_{\text{obsd}} = (E_{1/2})_\mu + (E_L) - (E_{1/2})_{\mu=0} - (E_L)_{\mu=0}$$

The evaluation of the term $\ln a_w$ may be made from experimental osmotic coefficients, ϕ , since by definition

$$-\frac{1}{\nu} \log a_w = 0.00782m\phi$$

where ν is the total number of ions produced, in this case, by the inert electrolyte and m is the molality of the solution. Thus, eq. 10 becomes

$$(\Delta E_{1/2})_{\text{obsd}} = \frac{0.0591}{n} \left\{ \log y_{M(H_2O)_x^{n+}} + 0.00782x m \nu \phi \right\} \quad (11)$$

at 25°. Thus, utilizing eq. 11, and upon the numerical evaluation of $y_{M(H_2O)_x^{n+}}$ and ϕ , it becomes possible to estimate the effect of changing the ionic strength of the inert electrolyte on the observed half-wave potential.

Experimental

A Sargent Model XV recording polarograph utilizing the 1-v. span was used for recording all polarograms. The initial (starting) potential was measured by usual potentiometric techniques which permitted standardization of the voltage scale to ± 1 mv. Potentials were measured in reference to a saturated calomel electrode which made contact with the test solution *via* a sintered glass disk and a saturated potassium chloride-agar salt bridge. This reference electrode was periodically rebuilt in order to minimize contamination. All data were obtained at a temperature of $25 \pm 0.2^\circ$. Solutions were degassed for approximately 10 min. by bubbling nitrogen through them prior to recording the polarogram. The capillary used had a $m^{2/3}t^{1/6}$ value of 1.29 in saturated KCl at -0.5 v. *vs.* s.c.e. Correction for the iR drop across the cell was not necessary owing to the magnitude of the currents measured. Half-wave potentials were determined in the usual manner.

The use of a maximum suppressor was not considered necessary (see subsequent discussion) for the concentrations of cadmium, 1-3 mM, investigated. Solutions were prepared by usual analytical techniques from reagent grade chemicals.

Results and Discussion

The validity and utility of eq. 11 rests essentially on three factors. The order in which they appeared in the derivation are: (1) No ion-pair formation or complexation occurs in high ionic strength solutions of electrolytes, (2) the hydration parameter remains constant over wide ranges of ionic strength, and finally (3) the activity coefficient of the hydrated, reducible species may be approximated as a function of the ionic strength.

The reason for the choice of studying the polarographic reduction of cadmium in highly concentrated solutions of the alkali metal nitrates for this investigation has already been illustrated by DeFord and Anderson. They have stated that the magnitude of the voltage correction to the half-wave potential for cadmium, due to the weak mononitrate complex which

(4) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

(5) R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948).

is said to exist,⁶ is of the order of 1 mv. for the systems they investigated; the same correction would apply to this investigation since the similar systems, although in terms of molality instead of molarity, were investigated. These prior investigations have led these authors to believe that there is little or no ion-pair or complex formation occurring in these systems.

Stokes and Robinson,⁵ in their derivation of a one-parameter equation for the determination of the activity coefficients of highly concentrated salt solutions, have illustrated that the hydration parameter, in this case x , could be assumed to remain constant over wide ranges of ionic strength. In conjunction with this, Brasher and Jones,⁷ among others, have studied the reduction of cadmium in solutions of sodium sulfate ranging in concentrations from 0.1 to 1.96 N and in sulfuric acid solutions up to 18 N . They observed, as did these authors in the present study, that the diffusion current was approximately linear with respect to the square root of the viscosity of the solution as is predicted by the Stokes-Einstein equation. This has been interpreted as indicating that the nature of the diffusing species remains essentially constant over the range of concentrations investigated.

The practicality of eq. 11 depends on the numerical evaluation, or a suitable approximation, of the activity coefficient of the reducible, hydrated species. Single-ion activity coefficients have yet to be determined experimentally; they can, in theory at least, be estimated from the mean activity coefficient of the dissolved solute. The determination of such activity coefficients in mixed electrolytes, such as the systems which are encountered in polarography, presents even more problems.

In solutions of low ionic strength where the only important parameter is the total salt concentration, the Debye-Hückel theory suggests that the activity coefficients for similarly charged species are the same. Thus, the activity coefficient of the reducible species may be estimated from the mean activity coefficient of the inert electrolyte. However, in highly concentrated systems, there are other parameters which must be considered as well.⁵ The determination of the mean activity coefficients in solutions such as these is approached through other techniques.⁸ For systems involving only uni-univalent species, the estimation of the mean activity coefficient of a dilute solution of one electrolyte dissolved in a concentrated solution of another may be made by taking the square root of the product of the individual mean activity coefficients at the concentration corresponding to the total concentration of the mixture. Such an approximation does not appear to be valid for other than uni-univalent systems as is indicated for HCl-BaCl₂⁹ or HCl-SrCl₂¹⁰ mixtures. It appears, from the analysis of these data, that the mean activity coefficient of the dilute species is closer to the solute which possesses the higher mean value. From this, and relationships suggested by the Debye-Hückel theory, the activity

(6) E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

(7) D. M. Brasher and F. R. Jones, *ibid.*, **42**, 775 (1946).

(8) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, Chapter 15, pp. 432-456.

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1958, p. 751.

(10) H. S. Harned and T. R. Paxton, *J. Phys. Chem.*, **57**, 531 (1953).

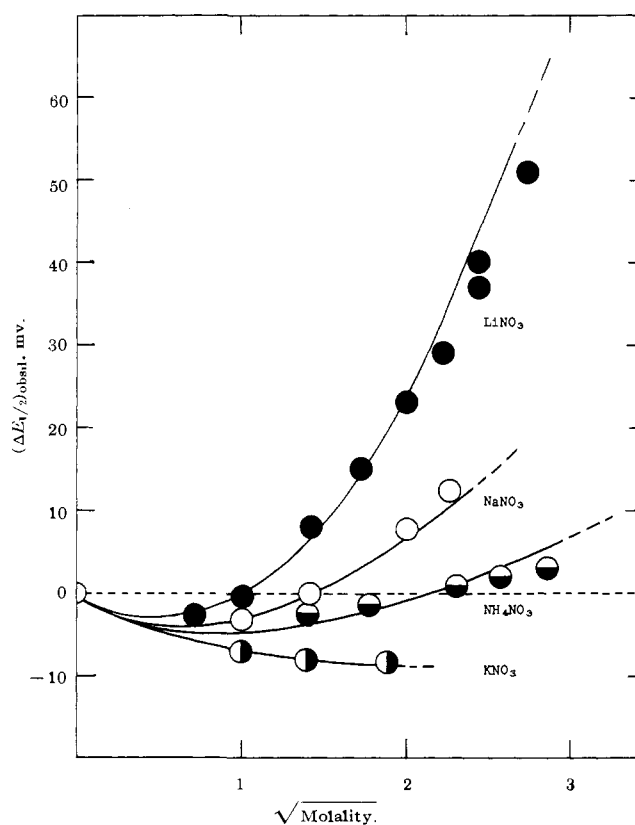


Fig. 1.—Comparison of experimental changes in the half-wave potential of cadmium in uni-univalent nitrate inert electrolytes as a function of molality with those predicted by eq. 12. The circles give the experimental values.

coefficient of the reducible species was approximated as being equal to the mean activity coefficient of the inert electrolyte (which in many instances was greater than the mean value for the reducible "salt" Cd(NO₃)₂). As the result of such an approximation, eq. 11 reduces to

$$(\Delta E_{1/2})_{\text{obsd}} = \{29.5 \log \gamma_{\pm} + 4.62m\phi\} \text{ mv.} \quad (12)$$

at 25° where γ_{\pm} is the mean molal activity coefficient of the inert electrolyte, ϕ is the osmotic coefficient for the solution of molality, m , specified, and $0.00782 \cdot [0.0591 \nu x / n]$ is equal to 4.62 when $x = 10$, $\nu = 2$, and $n = 2$. A hydration parameter of 10, for the hydrated cadmium ion, was found to give the best theoretical-experimental fit of the data except in the case of NaNO₃ where a value of 12 was used. This choice for the hydration parameter compares favorably with the value of 12 determined from compressibility data.¹¹ (If the activity coefficient of the hydrated cadmium ion were assumed to be $\sqrt{\gamma_{\pm \text{Cd(NO}_3)_2} \cdot \gamma_{\pm \text{LiNO}_3}}$, which is known to be too small, a constant difference between the predicted and experimentally evaluated $(\Delta E_{1/2})_{\text{obsd}}$ is only 3 mv. and approaches the accuracy of the measurement.)

The results of this investigation are given in Fig. 1 and Table I. The value for $(E_{1/2})_{\mu=0}$ vs. s.c.e. was found by extrapolation and is given as -0.572 v. (except for NaNO₃ systems where a value of -0.569 v. was determined). Although half-wave potentials for systems of ionic strength less than 1 molal are not reported, they were determined and agree with results from eq. 12; $(E_{1/2})_{\mu=0.1}$ for all cases was found to be -0.576 ± 0.002 v. vs. s.c.e. Experimental and calculated values for $(\Delta E_{1/2})_{\text{obsd}}$ are illustrated in Table I.

(11) R. A. Robinson and R. H. Stokes, ref. 8, p. 62.

TABLE I

THE EFFECT OF CONCENTRATION OF THE INERT ELECTROLYTE ON THE HALF-WAVE POTENTIAL OF THE REDUCIBLE SPECIES^a

Inert electrolyte	<i>m</i>	<i>M</i> ^b	Activity coeff. ^c	Osmotic coeff.	$-E_{1/2}$, mv.	$\Delta E_{1/2}$, mv.		Slope, mv./ <i>m</i>	
						Exptl.	Calcd.	Exptl.	Calcd.
LiNO ₃	0	0	572	0	0		
	0.5	0.5	0.726	0.954	574	-2	-2		
	0.9	0.9	0.737	0.987	574	-2	0		
	1.1	1.0	0.750	1.006	572	0	1		
	2.0	1.9	0.835	1.088	564	8	8		
	2.5	2.3	0.896	1.134	559	13	12		
	3.0	2.8	0.966	1.181	557	15	16		
	4.1	3.6	1.143	1.280	549	23	26		
	5.0	4.3	1.310	1.352	542	30	35		
	6.0	5.0	1.506	1.420	535	37	45		
6.1	5.1	1.526	1.427	532	40	46	7.7	9.4	
7.6	6.0	1.800	1.519	521	51	61			
8.6		2.095	1.571	517	55	71			
NaNO ₃	0	0	569	0	0		
	1.1	1.0	0.539	0.848	572	-3	-3		
	2.1	2.0	0.474	0.824	568	1	0		
	3.1	2.8	0.434	0.809	561	8	4		
	4.1	3.7	0.406	0.796	561	8	6	3.7	3.3
	5.1	4.4	0.384	0.788	556	13	10		
NH ₄ NO ₃	0	0	572	0	0		
	0.5	0.5	0.582	0.855	579	-7	-5		
	1.0	1.0	0.504	0.823	579	-7	-5		
	1.4	1.3	0.464	0.803	580	-8	-5		
	3.2	2.8	0.364	0.740	573	-1	-3		
	5.4	4.3	0.293	0.681	571	1	1	1.7	1.7
	6.6	5.0	0.268	0.660	570	2	4		
	8.2	5.8	0.242	0.637	569	3	6		
KNO ₃	0	0	572	0	0		
	0.1	0.1	0.739	0.906	576	-4	-4		
	0.5	0.5	0.545	0.817	576	-4	-6		
	1.0	1.0	0.443	0.756	578	-6	-7		
	2.0	1.9	0.333	0.669	579	-7	-8	-1	-0.8
	3.0	2.7	0.269	0.602	580	-8	-9		

^a Conditions: 1.0 mM Cd(NO₃)₂, no gelatin, s.c.e. reference electrode. ^b Calculated from equations given in ref. 9, p. 725, and from "International Critical Tables," 1st Ed., Vol. III, p. 59. ^c Osmotic and mean activity coefficients were obtained from data given in ref. 8.

It was noted that a plot of $(\Delta E_{1/2})_{\text{obsd}}$ vs. molality of the inert electrolyte yielded a linear relationship above concentrations of 1 *m* and the experimental and theoretical slopes for these lines are also given in Table I. It was felt that comparison of these slopes would place less importance on the determination of $(E_{1/2})_{i=0}$ and that any possible contamination effect would be lessened.

In the previous investigation of DeFord and Anderson,² solutions were prepared containing 0.001% gelatin. In order to eliminate gelatin as a possible variable in this investigation, these authors performed several preliminary experiments in order to determine if the use of gelatin was necessary. Solutions of polarographic concentrations of cadmium in 1–9 *m* concentrations of LiNO₃ were run with and without 0.005% gelatin. The half-wave potential of cadmium was identical, within experimental error, over the entire concentration range of LiNO₃ investigated; a plot of $E_{1/2}$ vs. molality of LiNO₃ without gelatin yielded a slope of 7.7 as compared to 7.9 mv./molal LiNO₃ with 0.005% gelatin. Similar point checks on 5.1 *m* NaNO₃, 8.2 *m* NH₄NO₃, and 3.0 *m* KNO₃ yielded $E_{1/2}$'s for cadmium of -0.556, -0.569, and -0.580 v. without gelatin as compared to -0.557, -0.569, and -0.580 v. with gelatin vs. s.c.e., respectively. It was interpreted from

these results that the same conclusions could be drawn from either system, and maxima of the second kind, if present, did not affect the validity of the experimental values.

Calculation of the slope of the line obtained from plotting $E_{d.e.}$ vs. $\log [i/(i_d - i)]$ ranged from 28 to 32 mv. for all polarograms listed in Table I. This indicated that a reversible two-electron reduction for cadmium was observed in all cases.

It might be noted that eq. 12 begins to deviate from the experimental for systems of LiNO₃ above concentrations of 4 *m*. It has been pointed out previously⁵ that as *mv* approaches a value of 10–15, the assumption of a constant hydration parameter begins to fail because the "competition" for water molecules becomes noticeable. When "stripping" of the water molecules from the reducible species does become important, a smaller hydration parameter (one which is a function of the molality) should be used. As a result, the theoretical $(\Delta E_{1/2})_{\text{obsd}}$ would be smaller than those listed in Table I and a better experimental-theoretical fit of the present data would result.

The agreement between the experimental and calculated values of $(\Delta E_{1/2})_{\text{obsd}}$ leads these authors to believe that eq. 11 and/or 12 could be of significant value in the polarographic investigation of solutions of vari-

able and/or high ionic strength. Though there may be many criticisms which may be expressed concerning these equations, the empirical value is clear from the results illustrated in the data presented. These results seem to justify the arguments set forth in the derivation. Other systems such as mixed uni-uni- and di-univalent ($\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, etc.) inert electro-

lytes as well as noncharged reducible species have been investigated and are to be presented in subsequent communications.

Acknowledgment.—These authors wish to express appreciation to Sigma Xi and the Mead-Johnson Research Center for their partial support in this investigation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

The Structure of Crystalline Tetraphenylporphine. The Stereochemical Nature of the Porphine Skeleton^{1,2}

BY M. J. HAMOR, T. A. HAMOR, AND J. L. HOARD

RECEIVED NOVEMBER 21, 1963

Analysis of all three-dimensional X-ray diffraction data photographically recordable with Cu $K\alpha$ radiation from tetragonal single crystals of tetraphenylporphine provides a definitive description of the atomic arrangement. The space group is $I4_2d$, the required molecular symmetry is S_4 , and "half-atom" peaks for hydrogen attached to nitrogen are clearly resolved by Fourier difference synthesis; the implication that stacking disorder does not seriously affect accuracy is supported also by other evidence, e.g., the high yield of observable reflections, ca. 91% of theoretical. Bond lengths obtained for the porphine skeleton are thought to be the most accurate values thus far reported. Simple theory suggests that at sufficiently low temperature the equilibrium configuration of the unconstrained porphine skeleton is somewhat ruffled, but the energy barrier to reflection of configuration through the mean plane is so low that at ordinary temperatures the skeleton is quasi-planar and easily deformable. Thus a mutual accommodation of the observed ruffling of the porphine skeleton (Fig. 1) in crystalline tetraphenylporphine with the observed parallel stacking of quasi-planar molecules in the crystalline phthalocyanines is achieved.

Introduction

As a prelude to attack upon the structural problems encountered in the naturally occurring porphyrins, one attempts first to determine the stereochemical characteristics of the central porphine skeleton. X-Ray diffraction analysis of crystalline structure, with utilization of three-dimensional intensity data from good single crystals, can provide the needed fundamental information for subsequent theoretical digestion. The classic determinations of structure for the crystalline phthalocyanines,³ achieved by X-ray zonal analysis, display essentially flat molecules tightly packed in parallel arrays; they provide bond parameters which, although lacking the authority of data now obtainable, are generally reasonable. Very recent determinations of crystalline structure for nickel etioporphyrin-I,⁴ copper tetraphenylporphine,⁵ and tetraphenylporphine⁶ itself assign markedly ruffled configurations to the porphine skeletons of the respective molecular species. The *a priori* grounds for anticipating easy deformation of the porphine skeleton normal to its mean plane—leading, indeed, to the conclusion that a somewhat ruffled or bent configuration should be stable for a free porphyrin molecule at sufficiently low temperatures—were outlined in the most recent communication⁶; this matter, together with the supporting experimental evidence, are to be further developed herein.

The bond parameters obtained from our three-dimensional analysis of *tetragonal* crystals of tetraphenylporphine afford, we believe, the most accurate stereochemical description of a porphyrin molecule thus far published. A virtually concurrent determination of structure for *triclinic* crystals of tetraphenylporphine carried out at Yale University has come recently to our attention.⁷ The two studies are in gratifyingly good agreement on all major points, although there are inevitably some differences (*vide infra*) at the center of the molecule; *i.e.*, in the disposition of the nitrogen atoms and the hydrogen atoms attached thereto. With some help also from the copper tetraphenylporphine study, it becomes feasible to appraise the importance of π -bonding in the porphine skeleton and in the molecule as a whole. A molecular orbital treatment of the bonding pattern in the porphine skeleton is simultaneously in progress.⁸

Experimental

The crystals of tetraphenylporphine used for determination of structure were kindly supplied by Adler and Shergalis.² The final stages of purification and of crystal growth were effected by carefully controlled techniques of vacuum sublimation.

The unit cell of tetragonal tetraphenylporphine has $a = 15.125 \pm 0.025$, $c = 13.94 \pm 0.02$ Å, and contains four molecules; the calculated and measured densities are, respectively, 1.28 and 1.27 g./cc. The X-ray symmetry is that of the point group D_{4h} -4/m, but tests for piezoelectricity are positive. Systematic vanishings of spectra⁹ are those demanded by the (non-centrosymmetric) space groups⁹ D_{2d} -12- $I4_2d$ and C_{4v} -11- $I4_1md$.

Three-dimensional X-ray data were recorded photographically on multiple films in a Weissenberg equi-inclination camera. The crystal specimen was a tetragonal bipyramid having diameters along a and c , respectively, of 0.35 and 0.32 mm. With a linear absorption coefficient of 7.0 cm^{-1} for Cu $K\alpha$ radiation, no

(1) Supported by the U. S. Public Health Service, the National Science Foundation, and the Advanced Research Projects Agency. We thank also the Staff of the Cornell Computing Center, Mr. R. C. Lesser, Director.

(2) The very pure crystals of tetraphenylporphine used in our study were supplied by A. A. Adler and W. Shergalis, Department of Chemistry, University of Pennsylvania, with support from the U. S. Signal Corps (Grant DA-SIG-36-039-61-G9).

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 236 (1940).

(4) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963).

(5) E. B. Fleischer, *ibid.*, **85**, 1353 (1963).

(6) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *ibid.*, **85**, 2334 (1963).

(7) A. Tulinsky, private communication.

(8) H. Kobayashi and M. Gouterman, private communication.

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