

Table III. Calculation of α in the Ground and First Excited Singlet States^a

Substituent	σ_1^b	α	α^*
F	+0.50	0.31	0.8
Cl	+0.47	0.37	0.8
Br	+0.45	0.25	0.6
OCH ₃	+0.23	0.28	0.6
CH ₃	-0.05	0.26	0.5

^a Using $\rho_1 = 2.229^{16}$; $\rho_1^* = 3.62$ from eq. 4. ^b Reference 22.

actions at *meta* positions are nearly as important as those at *para* positions.

A correlation between triplet-state acidities and ground-state σ values has also been made. Table II lists the pK_a^T values obtained from phosphorescence spectra. The least-squares line for a plot of pK_a^T vs. σ

(Figure 3) is

$$\log \left(\frac{K_x}{K_0} \right)^T = 1.72\sigma + 0.04 \quad (12)$$

with $\rho = 1.72$ and $r = 0.79$. However, the difference between the triplet- and ground-state acidity constants is so small that uncertainties in the determination of spectroscopic frequencies are much more significant in this case than for the lowest singlet state. Hence, other than demonstrating a statistically significant Hammett correlation in the lowest triplet state, no further treatment of the triplet-state data was attempted.

Acknowledgment. The authors wish to thank L. P. Hammett for helpful discussions.

Successive One-Electron Reduction Potentials of Porphins and Metal Porphins in Dimethylformamide

D. W. Clack and N. S. Hush

Contribution from the Department of Inorganic Chemistry, University of Bristol, Bristol 8, England. Received May 26, 1965

The reduction of a number of porphins, including tetra-benz- and tetraazaporphins, and their metal complexes, has been studied at a dropping mercury electrode in dimethylformamide. Either three or four one-electron steps are found, corresponding to the formation of mono-, di-, tri-, and tetranegative porphin ions. The disproportionation free energies of the ions are positive and (for a given ion charge) remarkably constant. Some aspects of the electronic structures of the porphins and of the metal complexes are discussed in the light of these results.

Introduction

The negative ions of a number of porphin, tetra-benzporphin, azaporphin, and phthalocyanine molecules and metal complexes have been prepared in 2-methyltetrahydrofuran solution by reduction with sodium metal.¹ The formation of the negative ions of zinc $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin by reduction with sodium benzophenone ketyl and sodium anthracene has also been studied in tetrahydrofuran solution.² Quantitative experiments showed that both mono-negative and dinegative ions were formed.

These ions—and perhaps ions in still more negative oxidation states—should also be formed by reduction of the porphins at a cathode in an aprotic solvent. In order to investigate this, we have examined the reduction steps of a number of porphins at a mercury electrode in dimethylformamide solution. Closs and Closs² have reported a two-step reduction of zinc $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin. Apart from this and some recent work³ using aqueous solutions (yielding tetrahydroporphins as final reduction products), porphin reduction does not seem to have been much studied at

electrodes. This work forms part of a general investigation of the formation and properties of porphin ions.

Experimental Section

Current-potential measurements were made using a three-electrode cell at $20 \pm 1^\circ$. The dropping mercury electrode had a flow rate of 1.50 mg. sec.⁻¹ and a drop time of 4.0 sec. on open circuit. The anode was a mercury pool, and a saturated aqueous calomel electrode was used as a reference. The junction of the reference electrode and the solution was made through a ground-glass sleeve fitting the tapered end of the side arm of the calomel half-cell. No diffusion of water through this junction could be detected in the reduction experiments over periods of at least 2 hr.

The potential of the cathode was measured to ± 1 mv. using a Pye precision potentiometer. The current was determined by a null method, by backing off the potential drop resulting from the current flow across a precision resistor with an accuracy of $\pm 0.01 \mu\text{a}$. "White spot" nitrogen, which had previously been passed through a liquid nitrogen trap and a presaturator containing dimethylformamide and 0.1 *M* N(*n*-Pr)₄-ClO₄, was bubbled through the solution for 15 min. before each experiment to remove oxygen and was passed continuously over the surface of the solution during the run. Each set of current-potential measurements was rechecked after 2 hr. Good agreement was found for the half-wave potentials. For some molecules, the wave heights were larger after the solutions had been left for this time. This was due to a concentration increase, as some of the porphins were very slow to dissolve at room temperature. The solvent used in all experiments was dimethylformamide containing N(*n*-Pr)₄ClO₄ (0.1 *M*).

(1) N. S. Hush and J. W. Dodd, *J. Chem. Soc.*, 4607 (1964).

(2) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 818 (1963).

(3) A. Ricci, S. Pinamonti, and S. Bellavita, *Ric. Sci.*, **30**, 2497 (1960).

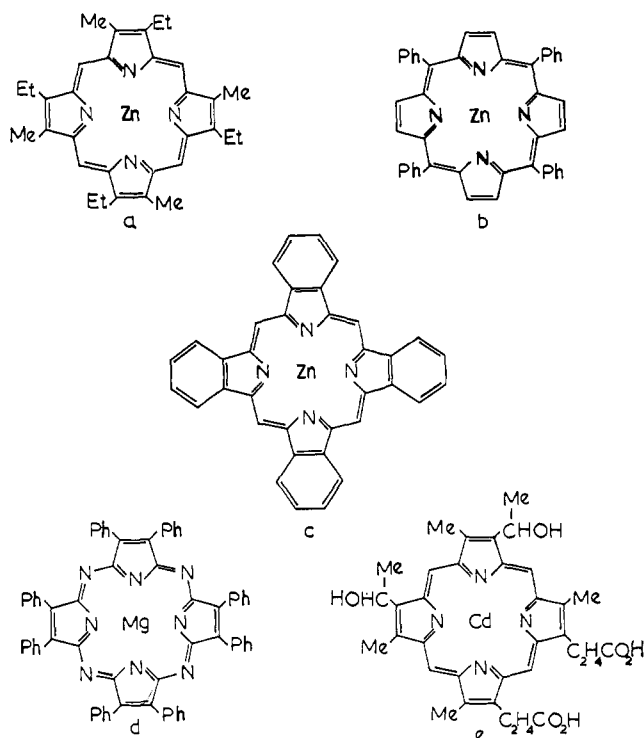


Figure 1. Structures of some porphyrin ring systems in compounds examined: (a) etioporphyrin I, (b) $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin, (c) tetrabenzporphyrin, (d) octaphenyltetraazaporphyrin, (e) haematoporphyrin.

The porphyrins and their complexes were in general found to be sparingly soluble in dimethylformamide, and the saturated solution was often used. Concentrations were of the order of 10^{-3} – 10^{-4} M. Phthalocyanine and the few metal phthalocyanines that were available were unfortunately too insoluble to be studied by the present techniques.^{3a}

Particular care was taken to make sure that the molecule being reduced was correctly identified. For this purpose, the absorption spectra of the solutions were examined immediately after completion of the current-potential measurements. This precaution is important, as many of these molecules react with traces of acid or alkali. Thus, for example, $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin dissolves in dimethylformamide quantitatively and instantly loses the central protons on addition of a drop of a solution of $N(n\text{-Pr})_4\text{OH}$ in aqueous dimethylformamide, and the $[\text{N}(n\text{-Pr})_4]_2$ salt of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin is formed. This salt, which does not appear to have been described previously, was identified by means of its typical $(\text{M}^1)_2$ salt of porphyrin spectrum, which closely resembled that of the disodium salt of this porphyrin⁴ (bands were found at 642, 592, 550 $m\mu$ and the Soret hand occurred at 444 $m\mu$). On addition of a few drops of formic acid to this solu-

(3a) NOTE ADDED IN PROOF. Reduction potential data for a series of metal phthalocyanines in dimethylformamide have now been obtained using a more sensitive differential technique: N. S. Hush and D. W. Clack, unpublished work.

Since this article was submitted, we have learned that Dr. R. S. Felton has also examined the reduction of a number of porphyrins in aprotic media: Thesis, Harvard University, 1964. Where comparison is possible, his results are in reasonable agreement with our measurements. We are indebted to Dr. M. Gouterman (Harvard University) for making a copy of the thesis available.

(4) Useful references to porphyrin spectra are given by M. Gouterman, *J. Mol. Spectry.*, **6**, 138 (1961).

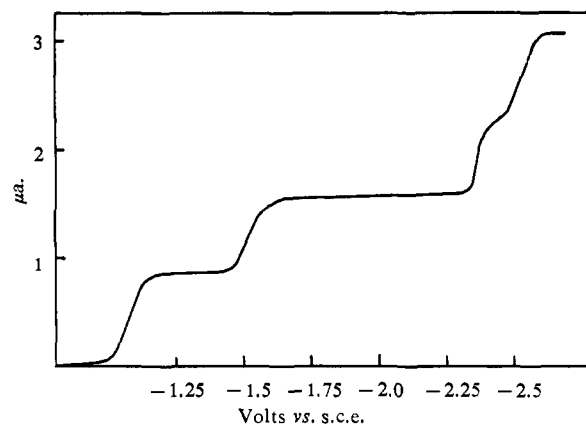


Figure 2. Current-potential curve for $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin in dimethylformamide containing 0.1 M $N(n\text{-Pr})_4\text{ClO}_4$.

tion $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin (pink) is re-formed and on further addition of formic acid, two further protons were added, giving the green dication of this porphyrin. The reduction of this last porphyrin could not be easily studied, owing to interference from hydrogen ion reduction (*vide infra*). Transition metal cations are fairly firmly bound. For example, Cu^{2+} was not displaced from copper etioporphyrin IV on addition of $N(n\text{-Pr})_4\text{OH}$. In all solutions, the species present could be identified unambiguously from the visible band system and the position of the intense Soret ultraviolet peak. These measurements were made using a Beckman DK-2 ratio-recording spectrophotometer.

Materials. Dimethylformamide (B.D.H.) was allowed to stand with occasional shaking for 3 days over anhydrous Na_2CO_3 in 250-ml. portions and was then distilled under reduced pressure. The fraction boiling in the range 38–41° was collected. Clean sodium metal and anthracene were added to the distillate forming disodium anthracene *in situ* in order to remove traces of water, acid, and oxidizing agents. The solution was left for a further 12 hr. Dimethylformamide was distilled from this solution under reduced pressure just before the commencement of a run.

$N(n\text{-Pr})_4\text{ClO}_4$ was prepared by quantitative precipitation from the aqueous hydroxide solution (Eastman Kodak) with perchloric acid. It was recrystallized three times from dimethylformamide and dried under vacuum.

The porphyrins were research samples which have been described previously¹ and were all spectrally pure. The structures of the ring systems examined are shown in Figure 1.

Results

Figure 2 shows a typical current-potential curve for $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin. Four reduction steps can be distinguished. The heights of these steps successively decrease, owing to the decrease in electrode drop time as the very negative potentials of the later steps were approached. The fourth step occurs near the decomposition potential of the solution (~ -2.8 v.). No adsorption effects (pre- or post-steps) were observed with this or any other porphyrin studied. Also, no dependence on concentration was noted over the limited concentration range available.

The first reduction step is identified as a one-electron addition by analogy with the course of the reaction

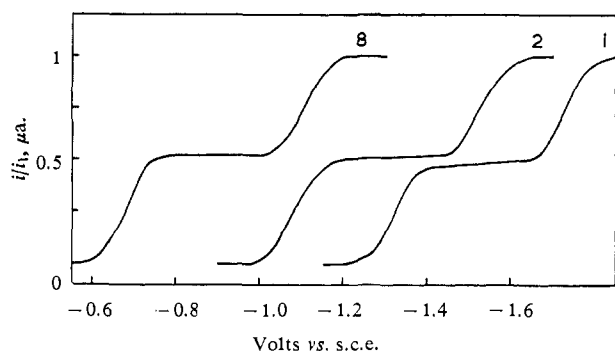


Figure 3. Current-potential curves for first and second one-electron reduction steps of zinc tetraphenylporphin (1), $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin (2), and magnesium octaphenyltetraazaporphin (8). Numbering of porphins is that of Table I.

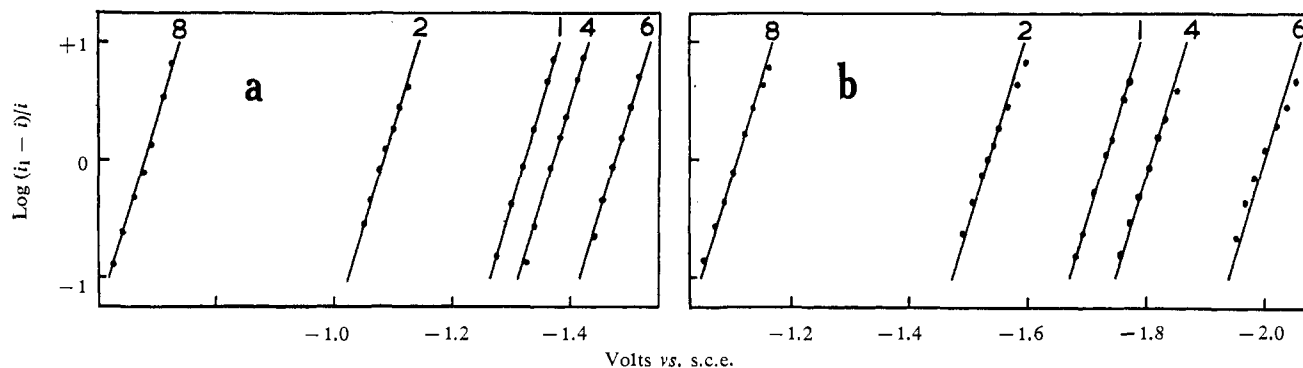


Figure 4. Analyses of current-potential curves for (a) first reduction step and (b) second reduction step. Numbering of porphins is that of Table I. The straight lines are drawn with the theoretical slope 0.0592 v.

with sodium, from which it is known that the mononegative ion is stable to disproportionation provided that hydrogen ion is absent. As the three remaining steps, when corrected for the drop-time factor $t^{1/2}$, have identical heights, these also represent successive one-electron additions. The lowest vacant orbital in this molecule is doubly degenerate (symmetry e_g in D_{4h}), and we assume that the reduction steps correspond to the stepwise filling of this level to its complement of four electrons.

The half-wave potentials of the successive steps are listed in Table I. The general result for the series of molecules studied is that either three or four one-electron reduction steps are found in the accessible potential range. Four steps are seen when the first reduction potential $E_{1/2}(1)$ is not too negative (> -1.4 v.). For molecules with first reduction potentials more negative than this, the third step occurs near the solvent decomposition potential, and the fourth step is

Table I. Porphin Reduction Potentials (v.) in Dimethylformamide Containing 0.1 M $N(n\text{-Pr})_4\text{ClO}_4$, Referred to Saturated Aqueous Calomel Electrode at 20°

No.	Porphin	$-E_{1/2}$ (1)	$-E_{1/2}$ (2)	$-E_{1/2}$ (3)	$-E_{1/2}$ (4)
1	Zn $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin	1.32	1.73	2.45	2.67
2	$\alpha,\beta,\gamma,\delta$ -Tetraphenylporphin	1.08	1.52	2.38	2.53
3	$[N(n\text{-Pr})_4]_2 \alpha,\beta,\gamma,\delta$ -tetraphenylporphin	1.45	1.87	2.26	2.44
4	Etioporphyrin I	1.37	1.80	2.67	
5	Zn etioporphyrin I	1.62	2.00	2.77	
6	Cu etioporphyrin IV	1.48	1.99	2.70	
7	Zn tetrabenzoporphin	1.47	1.84	2.49	2.70
8	Mg octaphenyltetraazaporphin	0.68	1.11	1.81	2.18

presumably masked. This behavior is found with etioporphyrin I, zinc etioporphyrin I, and copper etioporphyrin IV (no. 4-6 in Table I). For these molecules, the first step occurs at -1.37 , -1.62 , and -1.48 v., and the third step at -2.67 , -2.77 , and -2.70 v., respectively.

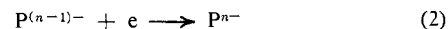
The reduction processes are evidently remarkably similar for the species examined, in spite of the variety of substituents on the periphery of the porphin skeleton and on the central nitrogen atoms and with aza-substituted *meso* positions.

The electrode reactions comprise electron transfer to large aromatic molecules and would be expected to be rapid. In agreement with this, analysis of the first two reduction steps shows that the current is almost entirely diffusion-controlled for those molecules which

were sufficiently soluble for a sufficiently detailed current-potential plot to be possible. (The $N(n\text{-Pr})_4$ salt of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin is an exception and is discussed separately below.) Some typical curves and analyses are shown in Figures 3 and 4.⁵ The gradients of the plots of E against $\log [(i_1 - i)/i]$ are very close to the theoretical value (0.0592) for diffusion-controlled currents. Accordingly, the half-wave potentials $E_{1/2}(n)$ ($n = 1, 2, 3, 4$) for these steps can be set equal to

$$E_{1/2}(n) = E_0(n) + \frac{RT}{F} \ln \left\{ \frac{f_{(n-1)} D_n^{1/2}}{f_n D_{(n-1)}^{1/2}} \right\} \quad (1)$$

where $E_0(n)$ is the formal potential for the reaction



and f_2 and D_2 are the activity coefficient and diffusion coefficient, respectively, for a species of charge $-Ze_0$. The second term on the right-hand side of eq. 1 is probably very close to unity and will not be further considered here.

The third and fourth reduction steps will not be analyzed in detail, as the limiting currents were not as well defined, and the shapes of the waves suggest that reaction with the solvent is occurring to a small extent. Here also, however, the $E_{1/2}(n)$ values are probably close to the formal potentials $E_0(n)$.

Owing to the low concentrations of most of the porphin solutions, small amounts of reducible impurities in the base solution sometimes caused difficulties. In particular, a small hydrogen ion reduction

(5) There is evidence for small departures from reversibility for some of these systems, which will probably make possible determination of the rate constants of the electron-transfer steps. We hope to examine these in more detail.

step at ~ -2.0 v. due to traces of acid was occasionally present in the solution. This was identical in position with the step produced by addition of formic acid and disappeared on adding a small amount of $N(n\text{-Pr})_4\text{OH}$. This presumably resulted from slight hydrolysis of the dimethylformamide. If a porphin was found to exhibit a reduction step close to -2.0 v., the system was checked to make sure that this was not, in fact, due to a trace of acid. The second step for copper etioporphyrin IV, for example, occurs at -1.99 v. This remained on adding a trace of $N(n\text{-Pr})_4\text{OH}$, and so was a porphin reduction step. The second step of zinc etioporphyrin I occurred at -2.00 v., but here it was found that the small hydrogen reduction step could just be distinguished from that of the porphin. We believe that the second steps listed in the table are correctly identified as porphin reduction steps in all cases.

The current-potential curves of the $N(n\text{-Pr})_4$ salt of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin were exceptional, in that all four steps were drawn out and had somewhat ill-defined limiting currents. This must be connected with the fact that instead of a small divalent metal ion or protons, bulky tetraalkylammonium ions are loosely bonded to the central nitrogen atoms. The unreduced porphin can probably be represented here as $(M^+)_2P^{2-}$, and addition of one electron produces a species P^{3-} , associated with tetraalkylammonium ions. This has the same formal charge as the trinegative ion produced in the third reduction step of strongly bonded complexes. It is probable that the unusual shapes of the curves are largely due to somewhat slow electrode reactions in this case.

We mention finally that cadmium hematoporphyrin, which was sufficiently soluble to be examined, exhibited a first step at -0.64 v., and thereafter an ill-defined series of drawn-out steps. This behavior is due to the presence of carboxyl groups, resulting in interference by hydrogen ions.

Discussion

The electronic structures of porphins and their complexes have not been examined in detail. These results are of some interest in that they bring out some general features of these structures.

The lowest vacant orbital of the porphin molecule is the orbital from which the lowest conduction band is formed in the crystal. The energy of this orbital is seen to vary considerably over the range of structures studied. The value of $E_{1/2}(1)$, for formation of the mononegative ion, becomes more positive by nearly 1 v. on passing from zinc etioporphyrin I to magnesium octaphenyltetraazaporphin. If the solvation energies of the mononegative ions are roughly equal, as is likely to be the case, there is, therefore, a difference of 1 e.v. in the energies of the empty e_g orbitals of these molecules.

In Table II, we list theoretical binding energies ϵ for the vacant e_g orbitals in prototype molecules.^{6,7} Those are calculated from Hückel orbitals,⁸ with $\alpha_N - \alpha_C = 0.66\beta_{CC}$ and $\beta_{CC} = \beta_{CN}$; for the integral β_{CC} we have used the semiempirical value -2.39 e.v.

(6) J. W. Dodd, Thesis, Bristol University, 1963.

(7) N. S. Hush and J. W. Dodd, in press.

(8) More detailed calculations for porphin molecules, taking account of electron interaction, have been carried out and will be discussed elsewhere.

Table II. Binding Energy ϵ of Lowest Vacant Orbital in Anthracene and Porphins^a

	ϵ , e.v.
Anthracene	0.9899
Tetrabenzporphin	0.9004
Porphin	0.6862
$\alpha,\beta,\gamma,\delta$ -Tetraphenylporphin ($x = 1$)	0.5222
$\alpha,\beta,\gamma,\delta$ -Tetraphenylporphin ($x = 0.2$)	0.6773
Phthalocyanine	0.5999
Tetraazaporphin	0.2554
Octaphenyltetraazaporphin ($x = 1$)	0.2522
Octaphenyltetraazaporphin ($x = 0.2$)	0.2553

^a This is the energy of the Hückel orbital calculated with $\alpha_N - \alpha_C = 0.66\beta_{CC}$ and $\beta_{CN} = \beta_{CC}$, expressed in e.v., using the semiempirical value -2.39 e.v. for β_{CC} . The parameter x is the ratio of the carbon-carbon resonance integral across the bond linking the phenyl group to the porphin skeleton to the standard β_{CC} (data from ref. 6 and 7).

The value of ϵ for anthracene is included for comparison.

An approximate parallelism between the ϵ values and the first affinity of the molecules is to be expected. Phenyl groups attached to the porphyrin skeleton make little difference to the calculated orbital energies, particularly if (as is suggested by X-ray crystallographic studies⁹) the phenyl groups are forced to be normal to the plane of the ring, with little or no conjugation with the porphin system. A group of similarly substituted molecules is provided by the trio 8, 1, and 7. The order of increasing negative first reduction potential is magnesium octaphenyltetraazaporphin < zinc $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin < zinc tetrabenzporphin. This is qualitatively identical with the order of orbital binding energies of the prototypes, and the range of $E_{1/2}(1)$ (0.8 v.) is approximately the same as the change in ϵ (0.64 e.v.) of the prototypes. These variations in orbital energy are large, and the reduction potentials will evidently be very useful in providing relative values of $\epsilon(e_g)$.

A second and equally interesting feature of these results is the approximate constancy of the intervals ${}^{n-1}\Delta^n E_{1/2}$. Averaging over all data, we obtain

$$\begin{aligned} -{}^1\Delta^2 E_{1/2} &= +0.42 \pm 0.03 \\ -{}^2\Delta^3 E_{1/2} &= +0.75 \pm 0.06 \\ -{}^3\Delta^4 E_{1/2} &= +0.24 \pm 0.06 \end{aligned} \quad (3)$$

This near-constancy is remarkable. It is reasonable to

Table III. Reduction Potential Intervals for the Four One-Electron Steps (v.)

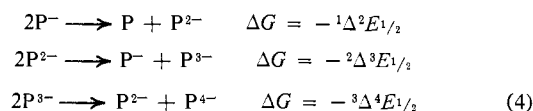
Porphin no. ^a	$-{}^1\Delta^2 E_{1/2}$	$-{}^2\Delta^3 E_{1/2}$	$-{}^3\Delta^4 E_{1/2}$
1	0.41	0.72	0.22
2	0.42	0.86	0.15
3	0.42	(0.39) ^b	(0.18) ^b
4	0.43	0.87	
5	0.38	0.77	
6	0.51	0.71	
7	0.37	0.65	0.21
8	0.43	0.70	0.37
	Av. 0.42 \pm 0.04	Av. 0.75 \pm 0.06	Av. 0.24 \pm 0.06

^a Porphins numbered as in Table I. ^b Irreversible (see text).

(9) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 1353 (1963).

conclude from this that substitution either of the central protons or in the porphin skeleton can be regarded as a one-electron perturbation, having the effect of shifting the one-electron orbital levels without appreciably affecting the eigenfunctions. It is particularly interesting that the metal porphins fit into this scheme. It might have been thought, for example, that electron addition to a Cu^{II}-substituted porphin would result in the Cu^{II} being progressively reduced to Cu^I and Cu⁰. However, it is evident that the level being filled is essentially a porphin orbital, the Cu remaining in the +2 state. This confirms conclusions drawn from examination of the electronic spectra of the mono- and dinegative metal porphin anions. In fact, the presence of Cu²⁺ or Zn²⁺ in the system appears merely to raise the energy of the vacant orbital by 0.1 or 0.24 e.v., respectively. This is less than the effect of octaalkyl substitution, which raises the vacant level of etio-porphyrin I 0.30 e.v. above that of $\alpha,\beta,\gamma,\delta$ -tetraphenylporphin.

The potential intervals measure the disproportionation energies of the negative ions. Thus



All negative ions are thus stable to disproportionation, with roughly constant free energies for a given state of ionization. This was predicted¹⁰ and subsequently confirmed¹¹ for the mono- and dinegative ions of aromatic hydrocarbons. Presumably the positive and nearly constant disproportionation energies in the porphin series have a similar origin: namely, electron repulsion terms outweighing the drop in potential energy due to increased solvation, the two compensating effects running parallel with change in molecular size.

Acknowledgment. We are indebted to the Department of Scientific and Industrial Research for a special grant for the purchase of the Beckman spectrophotometer and for a maintenance award to D. C.

(10) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(11) R. J. Hoijtink, E. de Boer, P. H. Van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

Reactions of Gaseous Ions. XVI. Effects of Additives on Ionic Reactions in Methane

M. S. B. Munson and F. H. Field

Contribution from the Esso Research and Engineering Company, Baytown Research and Development Division, Baytown, Texas. Received May 21, 1965

Studies are reported on the ionic processes occurring in the source of a mass spectrometer at pressures up to 2 torr for mixtures of CH₄ + 1% X, where X = Kr, Xe, O₂, NO, H₂O, and ND₃. The proton affinities of Kr and Xe are less than 118 kcal./mole since proton transfer from CH₅⁺ does not occur. Kr, Xe, O₂, and NO have very little effect on the distribution of product ions in methane, and the proton affinities of both O₂ and NO are less than that of CH₄. Water and ammonia produce major changes in the ionic distribution at 2 torr, since about 90% of the total ionization is composed of hydrated or ammoniated protons. Proton transfer from CH₅⁺ and C₂H₅⁺ to water and ND₃ is rapid. Rapid hydrogen-deuterium exchange is observed between ND₃H⁺ and ND₃, but exchange is not observed between ND₄⁺ and CH₄.

Introduction

In the earlier papers in this sequence,^{1,2} we have discussed the ionic reactions which have been observed in a mass spectrometer at pressures up to 2 torr for methane and mixtures of methane with ethane and propane. The previous results showed that small concentrations of other compounds could have major effects on the distribution of ions in methane at high pressures.

(1) F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 3289 (1965).

(2) M. S. B. Munson and F. H. Field, *ibid.*, **87**, 3294 (1965).

It is the purpose of this paper to extend the series of additives to different types of compounds in an effort to develop a systematic ionic chemistry.

We studied mixtures containing 1% Kr and 1% Xe, which are effectively inert with respect to reaction with the secondary ions of pure CH₄, and we were able to obtain upper limits for the proton affinities of these rare gases. The radical scavengers, O₂ and NO, were also studied as additives, and these proved to be unreactive as well. These observations are of particular importance concerning the inhibition of radiolyses by NO. The radiation-induced polymerization of certain olefins is strongly inhibited by trace amounts of H₂O or NH₃, and this inhibition has been interpreted in terms of chain termination by proton transfer to these strong bases.^{3,4} Consequently, we studied H₂O and ND₃ as additives to determine their effectiveness as proton acceptors.

Experimental Section

The mass spectrometer and experimental procedure have been described elsewhere.^{1,2} One modification was made for pressure measurements in some of these experiments: the McLeod gauge, which had been used previously, was replaced by a quartz spiral bourdon

(3) T. H. Bates, J. F. V. Best, and F. Williams, *Nature*, **188**, 469 (1960).

(4) M. A. Bonin, W. R. Busler, and F. Williams, *J. Am. Chem. Soc.*, **84**, 4355 (1962).