(5) (a) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 4332 (1976); (b) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *ibid.*, **98**, 5419 (1976); (c) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. L. Jorgensen, *Tetrahedron Lett.*, 3293 (1976).

(6) (a) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970); (b) M. J. S. Dewar and M. C. Kohn, *ibid.*, **94**, 2699 (1972); (c) L. J. Schaad, L. A. Burnelle, and K. P. Dressler, *Theoret. Chim. Acta*, **15**, 91 (1969); (d) L. J. Schaad, *Tetrahedron*, **26**, 4115 (1970); (e) J. A. Pople, R. Seeger, and R. Krishnan, unpublished calculations; (f) V. Staemmler, private communications; (g) C. E. Dykstra, *J. Am. Chem. Soc.*, **99**, 2060 (1977).

(7) W. R. Roth, G. Ruf, and P. W. Ford, *Chem. Ber.*, **107**, 48 (1974).

(8) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).

(9) J. Klein and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, **16**, 576 (1973). Li–π-allyl interactions in both components of the π system has been suggested by these authors to explain the structure of $C_3H_2Li_2$.

(10) M. Schlosser, "Struktur und Reaktivität Polarer Organometalle", Springer-Verlag, Heidelberg, 1973.

(11) M. L. Thompson and R. N. Grimes, *J. Am. Chem. Soc.*, **93**, 6677 (1971).

(12) In this context, it seems appropriate to quote R. N. Grimes (*Science*, **104**, 709 (1976)) on the 1976 Nobel Award to W. N. Lipscomb, "With carbon frequently assuming a coordination number of five or six, the carboranes constitute an extension of carbon chemistry which has profound (but not yet fully recognized) implications for the future directions of organic synthesis. Thus, the pyramidal molecules, $C_4B_2H_6$ and $C_3B_3H_7$ are in fact new kinds of organic heterocycles, albeit ones that have not yet penetrated the sanctums of standard organic textbooks. Sooner or later, it seems clear that organic chemists will have to come to grips with the revolution in our concept of the covalent bond that has been brought about through the medium of boron chemistry, so strongly influenced and guided by Lipscomb."

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A Four-Center, Concerted, Bimolecular Reaction: $ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI$

Sir:

The rate of the laser-induced chemical reaction
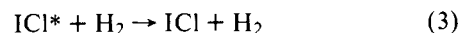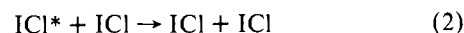
$$ICl^*(A^3\Pi_1) + H_2 \rightarrow HCl + HI \qquad (1)$$

has been measured as a function of ICl* vibrational energy. There is no dark reaction, but the reaction is promoted by water vapor, stopcock grease, metal surfaces, and stray light.[1] The kinetics appears similar to $I_2^* + H_2$,[2-4] and other reactions have been reported which involve electronic excitation of I_2.[5] The problem of four-center reactions has received considerable attention.[6]

ICl is prepared under vacuum from I_2 and Cl_2[7,8] and is never exposed to air. Mixtures of ICl (~5 or 9 Torr) and H_2 (10–600 Torr) are photolyzed for about 90 min in a 1-m-long, 5-cm-diameter quartz cell by a Chromatix CMX-4 flashlamp-pumped dye laser ($\Delta\nu = 0.3$ cm^{-1}) run at 30 pps. A calibrated thermopile monitors the laser power, which is 1.5 to 6 mJ per pulse in a 1-cm^2 beam. Approximately 60% absorption of the laser light is measured at $I^{35}Cl\ v'' = 0$ bandheads.

After photolysis all of the HCl, together with some residual Cl_2,[7] is distilled into a bulb with I_2 crystals. The Cl_2 reacts completely with the I_2, and the HCl is then redistilled. Its pressure is measured with a capacitance manometer, and mass spectra confirm that the product is HCl. HI and ICl react to form HCl and I_2; thus two molecules of HCl are formed in each reaction.

ICl* is removed by reaction 1 and by quenching:

Figure 1. Solid points are data without Ar, $P_{ICl} = 8.9$ Torr; the solid line is a fit to these points. The dashed line is the *predicted* yield with $P_{Ar}/P_{H_2} = 4.75$; open circles are corresponding data. Here, $P_{ICl} = 4.9$ Torr except for lowest P_{H_2}/P_{ICl} point, where $P_{ICl} = 8.9$ Torr (λ 616.8 nm, exciting 1200 cm^{-1} below dissociation).

Figure 2. Quantum yield vs. excitation energy. $P_{ICl} = 8.9$ Torr. The solid line is a fit to the data; the dashed line is a rough estimate of the effect of collisional dissociation. The point at 18 800 cm^{-1} was taken using a doubled YAG laser with 60-mJ, 20-ns pulses.

$$ICl^* + ICl \rightarrow ICl + ICl \qquad (2)$$

$$ICl^* + H_2 \rightarrow ICl + H_2 \qquad (3)$$

Fluorescence is much too slow to complete with reactions 1–3. The quantum yield for reaction is

$$\Phi = \frac{(HCl\ produced)/2}{photons\ absorbed} = \frac{k_1[H_2]}{k_2[ICl] + (k_1 + k_3)[H_2]} \qquad (4)$$

A Stern-Volmer plot of ICl* fluorescence lifetime vs. H_2 pressure gives $(k_1 + k_3) = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; similarly, Steinfeld[9] has measured $k_2 = 2.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; both are nearly independent of wavelength. k_1 is determined from the quantum yield, Figure 1. The solid curve is a least-square fit to the data using eq 4. Note that a two-parameter curve is fit with a single free parameter. The result, $k_1 = (9.0 \pm 0.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (90% confidence limits), corresponds to 9000 gas kinetic collisions. Assuming that the preexponential factor does not exceed the gas kinetic collision frequency, the activation energy is less than 5.5 kcal/mol. The reaction rate is quite large; the quantum yield is low because the quenching rate is even larger.

A single vibrational level of ICl* is excited initially, but vibrationally inelastic collisions spread the population distribution so that reaction may occur from other levels. The extent of this spread, which is limited by quenching, can be estimated
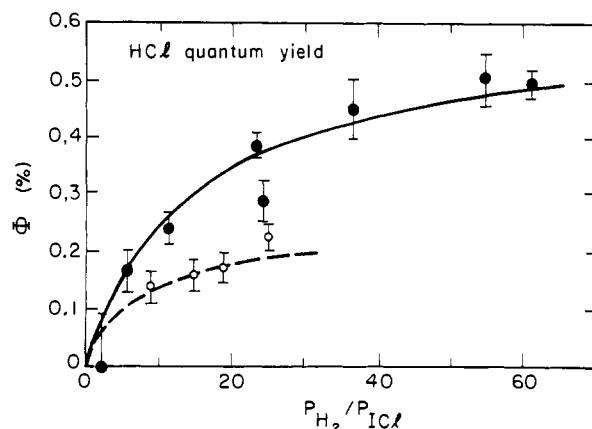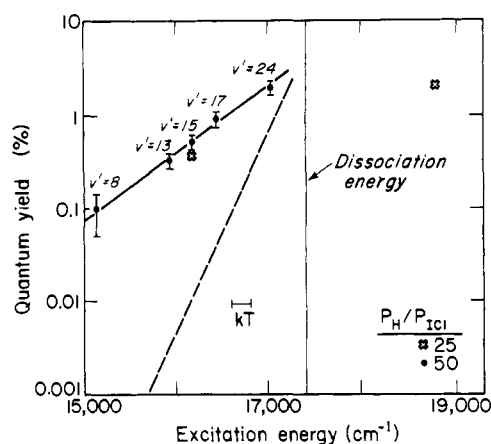
by comparison with the analogous $H_2-I_2^*(B^3\Pi_0, v' = 15)$ system.[10] Here, V–T events occur with a cross section of $\sim\frac{1}{6}$ gas kinetic. This is expected to be an upper limit to the V–T rate in ICl^*-H_2, since the energy level spacing in ICl^* is greater than that in I_2^*. The result is that $\sim75\%$ of the ICl^* which reacts does so from within three vibrational levels of the originally excited level. Figure 2 shows the quantum yield (proportional to k_1) as a function of the excitation energy. About 600 cm^{-1} (3 kT) of vibrational energy increases the rate constant by a factor of e.[11]

Halogen atoms, formed from sufficiently energetic collisions of ICl^*, could conceivably be contributing to the measured quantum yields. The dissociation probability, however, should decrease by $\sim1/e$ for each 200 cm^{-1} (kT) of vibrational energy,[12] dashed line in Figure 2. (Experiments[13,14] on $I_2(B^3\Pi_0)$ which seem to show higher dissociation quantum yields have not allowed for hot band absorption.) I atoms formed simply recombine, and Cl atoms are mostly scavenged by the fast reaction $Cl + ICl \rightarrow Cl_2 + I$;[15] when ICl is excited 1400 cm^{-1} above dissociation there is a low quantum yield of HCl (Figure 2), implying that, for excitation well below dissociation, radical reactions are not important. Finally, a quenching gas may be added to the system. Experiments with added argon at λ 616.8 nm ($v' = 15$) give quantum yields in very good agreement with those predicted from the measured quenching rate constant for ICl^* by Ar $(4.9 \pm 0.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (dashed line in Figure 1). These results prove conclusively that radicals are not important, since Ar should not inhibit their reactions, and that $ICl^*(A^3\Pi_1)$ is the reactive species.

The reactivity of ICl^* may be related to the fact that the dipole moment changes sign upon excitation[16] to I^-Cl^+. The positive Cl atom, with its partially filled valence shell, might be expected to be very reactive.

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References and Notes

(1) G. G. Palmer and E. O. Wiig, *J. Am. Chem. Soc.*, **74**, 2785 (1952), and references therein.
(2) G. M. Harris and J. E. Willard, *J. Am. Chem. Soc.*, **76**, 4678 (1954).
(3) T. A. Grover and J. E. Willard, *J. Am. Chem. Soc.*, **82**, 3816 (1960).
(4) L. C. Glasgow and J. E. Willard, *J. Phys. Chem.*, **77**, 1585 (1973).
(5) (a) V. I. Balykin, V. S. Letokhov, V. I. Mishin, and V. A. Semchishen, *Chem. Phys.*, **17**, 111 (1976); (b) F. Engelke, J. C. Whitehead, and R. N. Zare, "Faraday Discussions on Potential Energy Surfaces", Vol. 62, 1976, in press.
(6) D. L. King and D. R. Herschbach, *Faraday Discuss. Chem. Soc.*, **55**, 331 (1973), and references therein.
(7) G. V. Calder and W. F. Giauque, *J. Phys. Chem.*, **69**, 2443 (1965).
(8) R. E. Buckles and J. M. Bader, *Inorg. Synth.*, **9**, 130 (1967).
(9) G. W. Holleman and J. I. Steinfeld, *Chem. Phys. Lett.*, **12**, 431 (1971).
(10) R. Brown and W. Klemperer, *J. Chem. Phys.*, **41**, 3072 (1964).
(11) M. H. Mok and J. C. Polanyi, *J. Chem. Phys.*, **53**, 4588 (1970).
(12) A. Gelb, R. Kapral, and G. Burns, *J. Chem. Phys.*, **59**, 2980 (1973).
(13) T. W. Broadbent and A. B. Callear, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1367 (1972).
(14) D. H. Burde, R. A. McFarlane, and J. R. Wiesenfeld, *Phys. Rev. A*, **10**, 1917 (1974).
(15) M. A. A. Clyne and H. W. Cruse, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1377 (1972).
(16) F. E. Cummings and W. Klemperer, *J. Chem. Phys.*, **60**, 2035 (1974).
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## Imidazolate Complexes of Ferric Porphyrins

Sir:

The importance of imidazole as an axial ligand in hemoproteins is evident from the fact that histidine residues provide one or both axial ligands to iron in the majority of those proteins for which pertinent information is available.[1] Model studies of iron porphyrins have often been carried out using N-alkylimidazoles rather than imidazole itself, however, for a variety of reasons such as stability[2] or crystallizability[3] of the desired products. Recent studies of the binding of imidazole and N-alkylimidazoles to ferric porphyrins have established that their binding constants can differ by as much as 10^3.[4] These studies have also implicated hydrogen bonding of bound imidazole as a factor stabilizing ferric porphyrin–imidazole complexes.[4,5] Examination of published x-ray crystal structures of several heme proteins such as myoglobin,[6] cytochrome c,[7] and cytochrome b_5[8] reveals that histidylimidazoles bound to heme iron are hydrogen bonded to other residues on the polypeptide chain. Hydrogen bonding or actual deprotonation of
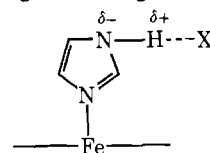

imidazole ligands provides a means whereby the tertiary structure of the protein could moderate the reactivity or redox potential of the iron center.[9] For this reason, we have undertaken an investigation of imidazolate (Im$^-$) complexes of ferric porphyrins, since deprotonation is the limiting case of strong hydrogen bonding of imidazole (ImH).
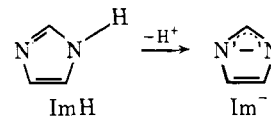
The bisimidazole complex $[Fe(TPP)(ImH)_2]^+$ (TPP, tetraphenylporphine) (**1**) is prepared by reaction of Fe(TPP)Cl with a large excess of ImH in several different solvents.[4] Titration of solutions of **1** in benzene, toluene, dichloromethane, and dimethyl sulfoxide with several different bases[10] (hydroxide, *tert*-butoxide, and imidazolate) results in virtually identical visible spectral changes. A titration with OH$^-$ in CH$_2$Cl$_2$ is shown in Figure 1. Stepwise addition of 1 equiv of OH$^-$ occurs with an isosbestic point at 585 nm. Further addition of hydroxide produces yet another species. The same spectral shifts and isosbestic point are observed for all three bases in CH$_2$Cl$_2$. We believe that we are observing the stepwise deprotonation of **1** as indicated in reaction 1.

$$1 \xrightarrow{-H^+} Fe(TPP)(ImH)(Im) \xrightarrow{-H^+} [Fe(TPP)(Im)_2]^- \quad (1)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$
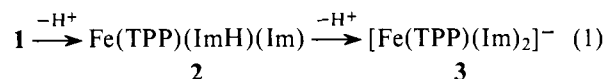
The bisimidazolate complex **3** can also be prepared by direct reaction of Fe(TPP)Cl with excess Im$^-$ in CH$_2$Cl$_2$ (eq 2).

$$Fe(TPP)Cl \xrightarrow{Im^-} 4 \xrightarrow{Im^-} [Fe(TPP)(Im)_2]^- \quad (2)$$
$$\mathbf{3}$$
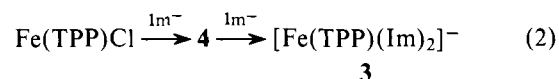
An intermediate **4** is observed in this reaction at low levels of Im$^-$. The blue shift of the Soret band of **4** relative to that of Fe(TPP)Cl, **1**, **2**, and **3** and the positions of the α,β bands imply that **4** is a high spin complex (see Table I). When reaction 2 is followed by EPR at 77 K, the typical high spin spectrum of Fe(TPP)Cl ($g = \sim6, \sim2$) disappears and no signal is observed for **4**.[11] Subsequent additions of Im$^-$ produce the low spin EPR spectrum of **3** ($g = 2.73, 2.28, 1.76$). We believe that **4** may be a high spin imidazolate bridged dimer such as $[(TPP)Fe-Im-Fe(TPP)]^+$.