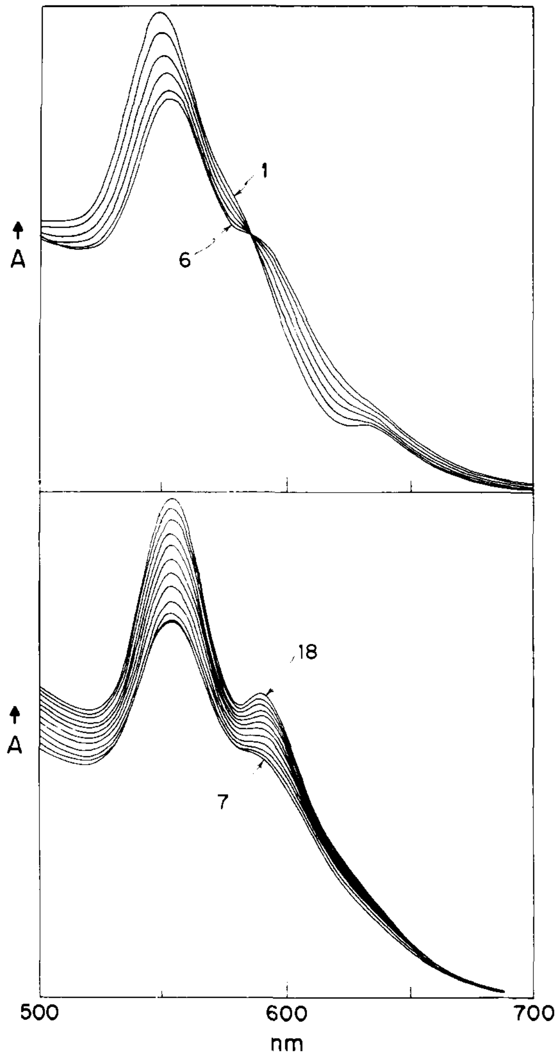

Figure 1. Titration of 3 mL of 10^{-4} M $FeTPP(ImH)_2^+$ in CH_2Cl_2 with 0.1 M Bu_4NOH in methanol/benzene by successive 0.5-μL additions. Six additions correspond to 1 equiv.

Table I

Compd	Visible absorption band positions, nm[a]		
$[Fe(TPP)(ImH)_2]^+$ (**1**)	416 (S)[b]	548	580 (sh)[c]
$Fe(TPP)(ImH)(Im)$ (**2**)	418 (S), 444 (sh)	552	585 (sh)
$[Fe(TPP)(Im)_2]^-$ (**3**)	425 (S), 444 (sh)	556	595
4	403 (S)	561	595 (sh)
$[Fe(TPP)]_2O$	406 (S)	569	612

[a] In CH_2Cl_2. [b] S, Soret band. [c] sh, shoulder.

Addition of acid to solutions of the deprotonated species **3** or **2** results in reversion of the visible spectra to that of the bisimidazole complex **1**. Addition of imidazole to solutions of the bisimidazolate complex **3** results in a shift of the spectrum to that of the monodeprotonated species **2**.

Attempts to isolate **2**, **3**, and **4** have been unsuccessful owing to precipitation of the insoluble polymer $[Fe(TPP)(Im)]_n$.[12] Solution susceptibility measurements have not been possible because of precipitation of the polymer at concentrations appropriate for NMR.

Addition of fluoride ion[13] to **1** results in spectral changes very similar to those observed upon addition of the three bases described above. These spectral changes have previously been attributed to hydrogen bonding of F^- to bound imidazole,[14] but our results and the high basicity of F^- in the gas phase[15] and in aprotic solvents[16] lead us to conclude that fluoride is essentially deprotonating bound imidazole.

Results similar to those described above are obtained upon titration of $Fe(PPIXDME)(ImH)_2^+$ with OH^- in CH_2Cl_2.[17] Singly and doubly deprotonated species are observed analogous to **2** and **3**. The monodeprotonated species has a visible spectrum very similar to that observed for the high pH form of the methemoglobin-imidazole complex.[18] The pK_a of imidazole bound to iron(III) in methemoglobin is known to have dropped from 14 to ~10 upon coordination.[18] This does not exclude the possibility, however, that strong hydrogen bonding or actual deprotonation of histidylimidazole ligands in ferric hemoproteins may occur at physiological pH in the nonaqueous hydrophobic cavity near the iron atom.

Further characterization of these imidazolate complexes and related species is continuing.

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Gas Phase Reactions of Anions with Nitrous Oxide and Carbon Dioxide

Sir:

Nitrous oxide and carbon dioxide are linear, isoelectronic molecules whose gas phase negative ion chemistry remains intriguing and important.[1] We wish to report that both species react readily with a variety of organic anions under the conditions of a flowing afterglow system. For N_2O the reaction process may be characterized as addition, followed by loss of H_2O, N_2, or CH_2O depending upon the nature of the anion;

carbon dioxide reacts primarily by simple addition. These processes pose interesting mechanistic problems and also serve as important sources of some new types of anions for further study in the gas phase.

In a flowing afterglow system,[2] ions are formed by sequential chemical reactions in a flowing helium stream ($\bar{v} = 80\ \mathrm{m\ s^{-1}}$, $P = 0.25$ Torr), sampled and analyzed by a quadrupole mass filter and detected by an electron multiplier. Allyl and substituted allyl anions were generated by proton abstraction by NH_2^- from propylene, isobutylene, 1-pentene, and 1-hexene. Nitrous oxide was added downstream. Reaction proceeded readily to give, as the major product, ions corresponding to addition of N_2O followed by loss of water. We formulate the process as shown in eq 1 and the resultant anion as a diazoalkene anion by analogy with diazo transfer reactions observed in solution.[3]

$$\begin{aligned}&RCH{=}CH\bar{C}H_2 + N{=}N{=}O\\ &\quad\rightarrow [RCH{=}CHCH_2N{=}NO^-]\\ &\quad\rightarrow [RCH{=}CH\bar{C}HN{=}N{-}OH]\\ &\quad\rightarrow [RCH{=}CHCH{=}N{=}N + OH^-]\\ &\quad\rightarrow RCH{=}CH\bar{C}{=}N{=}N + H_2O \qquad (1)\end{aligned}$$

The only mechanistic requirement, however, is that the reaction occur in an intermediate which decomposes to the diazoalkene anion and water. It is unlikely, for example, that the OH^--diazo complex dissociates with subsequent interaction of hydroxide with a different diazo neutral; neutral products of ion-molecule reactions exist in such low concentrations that collisions of these neutrals with ions essentially do not occur during the timescale of flowing afterglow experiments. Minor anionic products, corresponding to simple addition, were also observed as products of reaction 1.

An interesting process is the analogous reaction of the amide ion with N_2O to form the azide ion:[4]

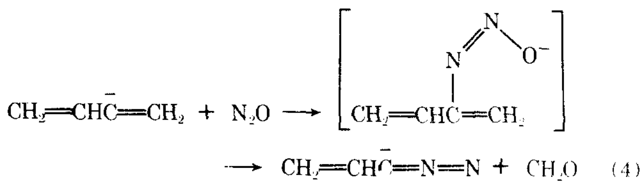
$$NH_2^- + N_2O \rightarrow N_3^- + H_2O \qquad (2)$$

We estimate that this reaction has a rate constant of $\sim 10^{-10}$ $\mathrm{cm^3\ s^{-1}}$, about an order of magnitude faster than that of the allyl anion. This indicates that a large fraction of the collisions result in reaction. The less basic anions $^-CH_2CN$ and $^-CH_2C_6H_5$ react similarly with N_2O but more slowly ($k \sim 10^{-13}\ \mathrm{cm^3\ s^{-1}}$). Still weaker bases, such as those produced by proton abstraction from acetone, acetaldehyde, ketene, acetylene, and *tert*-butyl alcohol, fail to react.

The phenide ion reacts with N_2O to give products at *m/e* 121 and 93. The higher mass corresponds to the simple adduct which, lacking α hydrogens, cannot react further to form the diazo anion. The second anion is presumably phenoxide ion formed by oxygen transfer:

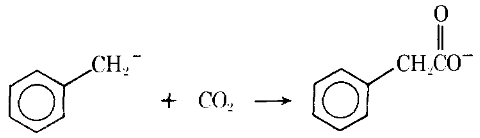
$$\begin{aligned}&C_6H_5^- + N_2O \rightarrow C_6H_5N{=}NO^-\\ &\qquad\rightarrow C_6H_5O^- + N_2\end{aligned} \qquad (3)$$

This latter species could arise by collapse of the simple adduct ($C_6H_5N_2O^-$) through a four-membered-ring intermediate or by a separate mechanism involving direct attack on the oxygen atom in nitrous oxide. Similarly, several other vinyl anions appear to react by oxygen transfer. In contrast, the anion formed by proton abstraction from 1,3-butadiene reacts with N_2O by addition followed by loss of formaldehyde:


(4)

The anionic product probably has the same structure as that produced in the direct reaction of allyl anion with N_2O. We have previously found that loss of neutral formaldehyde from an ionic reaction intermediate is a common process in anion-neutral encounters of organic species in the gas phase.[5]

In direct analogy with solution chemistry, carbon dioxide reacts with organic anions in the gas phase exclusively by addition to form carboxylate anions, for example,


(5)

The reactions are rapid for the anions generated by proton abstraction from propylene, isobutylene, 1-pentene, 1-hexene, butadiene, benzene, toluene, and *tert*-butyl alcohol. Moderate rates of addition are observed for the proton abstracted anions of acetone and acetonitrile while the anions of ketene, acetylene, and acetaldehyde react slowly. In all cases, the reactions of carbanions with CO_2 were faster than the corresponding reactions with N_2O. The process is formulated as nucleophilic addition rather than simple clustering since higher carbanion-CO_2 adducts were not evident under any conditions. Surprisingly, we have not found an organic anion which is inert to carbon dioxide in the gas phase.

The amide ion, however, exhibits an interesting and unique reaction with CO_2. Although the simple adduct is observed, the major product occurs at *m/e* 42, corresponding to the cyanate anion. The process may be formulated as addition of CO_2 with elimination of H_2O

$$NH_2^- + CO_2 \rightarrow NCO^- + H_2O \qquad (6)$$

in direct analogy with the amide-nitrous oxide reaction.[6]

The ion chemistry of carbon dioxide and nitrous oxide is of special interest since both species are important constituents of planetary atmospheres; their gas phase reactivity must therefore be understood for a complete description of atmospheric composition and processes.[7] However, most known atmospheric anions do not react efficiently with nitrous oxide, even though exothermic channels exist.[8] The apparent unreactivity of N_2O and the search for sinks of N_2O in the earth's troposphere is one of the most baffling current problems of atmospheric chemistry. The exponential increase in the use of fertilizers with subsequent denitrification and release of N_2O makes a clarification of the ion chemistry of N_2O essential. At the same time we hope that further studies will enable us to develop N_2O as a useful solution phase reagent. While solution analogs of the diazo transfer reactions with N_2O are known, yields are usually low and reaction conditions vigorous. The potentially extremely useful oxygen transfer reaction

$$R^- + N_2O \rightarrow RO^- + N_2 \qquad (7)$$

while greatly exothermic, has never been observed in solution.

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Far Red Photogalvanic Splitting of Water by Chlorophyll a Dihydrate. A New Model of Plant Photosynthesis

Sir:

Recently we have studied in detail the properties of P700, the chlorophyll a monohydrate dimer (Chl $a\cdot H_2O)_2$, on the basis of in vitro Chl a–H_2O interactions.[1-4] In this communication, we describe the observation of hitherto unreported Chl a photogalvanic water splitting reactions that result from photoactivation of the C-9 keto-linked chlorophyll a dihydrate aggregate (Chl $a\cdot 2H_2O)_n$.[2a,5]

We made use of the recently developed[6] Chl a photogalvanic cell in the study of Chl a–H_2O photoreactions. The experimental assembly, which has been described previously,[6] consists of two half cells (1) separated by a salt bridge. $LiClO_4$ or KCl was the electrolyte. The Chl a was plated on a Pt electrode from a 10^{-4} M solution in undried 2,2,4-trimethylpentane by a procedure similar to that described by Tang and Albrecht.[7] Film thicknesses corresponding to $\leq 10^{14}$ Chl a molecules cm^{-2} were employed. The content of dissolved oxygen in the cell assembly was controlled in the usual manner.[6] The pH values of the half cells were maintained using citric acid–NaH_2PO_4 buffer solutions in the pH 2–8 range, and NaOH–$NaHCO_3$ at pH >8. Upon illumination of the chlorophyll, a positive photopotential is developed at the Chl a–Pt electrode, generating a flow of electrons that originates from the Chl a free half cell,

$$Pt|Chl\ a{:}H_2O||H_2O|Pt \qquad (1)$$

The photochemical action spectrum of the freshly prepared Pt–Chl a electrode shows an approximately equal distribution of the observed photocurrent in two bands with maxima at 673 and 740 nm, respectively (see Figure 1A (a) of ref 6b). The latter band is attributed to the dihydrate polymer (Chl $a\cdot 2H_2O)_n$.[2a,d,6b] The 673-nm band has been ascribed to a Gaussian envelope of monomeric and dimeric complexes of chlorophyll a monohydrate.[6b] The photogalvanic action of a rigorously deoxygenated cell is predominantly transient in nature. A large part (~90%) of the observed photogalvanic current decays exponentially (half-life time ~1 s) under steady illumination conditions. The photocurrents recorded in Figure 1 correspond to the initial (t 0) readings. When the light is switched off, a reverse photocurrent of the same magnitude is observed. In this case, the observed reversible photogalvanic effects lead to no net photochemical change in the two half cells. These effects appear to be related to the reversible "phototropic" bleaching effect described by Rabinowitch[8] and Livingston.[9]

A minor (~10%) time-independent component in the photogalvanic action is also observed. This component is absent in the dark cycle and signifies an irreversible photoinduced redox reaction between the two half cells due either to unintentional impurities or, in view of the chemical constituents of 1, to the Chl a sensitized half cell reactions

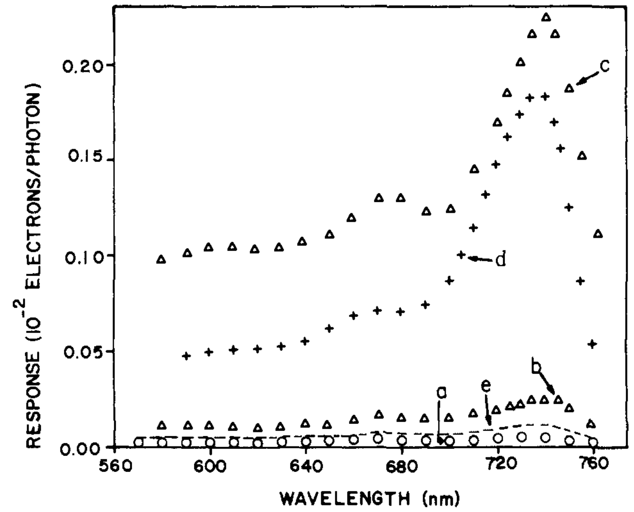

Figure 1. The Fe^{2+} photogalvanic enhancement effect of a freshly prepared Chl a–Pt sample: (a) before Fe^{2+} addition at pH 7, action spectrum consisting of two approximately equal bands at 673 and 740 nm (see Figure 1A (a) of ref 6b for the same spectrum on an expanded scale). (b) at pH 5 in Chl a half cell and pH 7 in Chl a free half cell; (c) at pH 3 in Chl a half cell and pH 7 in Chl a free half cell; (d) after addition of Fe^{2+} (10^{-3} M) in a; (e) at pH 7 in Chl a half cell and pH 11 in Chl a free half cell in the absence of divalent cations. The predominance of the 740-nm band in the enhanced action spectra underscores the critical role of (Chl $a\cdot 2H_2O)_n$ in the water splitting reactions 2 and 3. The action spectra a–e are measured from the initial (t0) readings of the photogalvanic response. The corresponding spectra for the irreversible component of the photogalvanic response are lower in intensity by a factor of two to ten, depending on experimental conditions (see text), but are essentially indistinguishable from spectra a–e in spectral distributions.

$$\text{Chl a–Pt photocathode:}\quad 2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad E_0 = -0.42\ V \qquad (2)$$

$$\text{Chl a free anode:}\quad 2H_2O \rightarrow 4H^+ + O_2 + 4e \qquad (3)$$

$$E_0 = -0.81\ V$$

We thus envisage reaction 2 as the electron acceptor in the photooxidation of the chlorophyll. The radical cation of the oxidized chlorophyll is then reduced to the neutral state by the oxidation of water in (3).

To establish the possible implication of reactions 2 and 3 in photogalvanic conversion, we have made the following observations. (i) The photocurrent increases dramatically with decreasing pH of the Chl a half cell (Figures 1a–c). (ii) The photocurrent is also enhanced by the introduction of Fe^{2+} ions in the Chl a half cell (Figure 1d). The observed effect increases with increasing concentration of Fe^{2+}. The steady-state operation of the photogalvanic cell results in the precipitation of $Fe(OH)_2$. Similar enhancement effects are also observed when Ba^{2+}, Ca^{2+}, and Zn^{2+} ions are added in the Chl a cell. (iii) On enhancement of the photogalvanic response in i and ii, the time-independent component of the observed steady-state photocurrent also becomes significantly enhanced, being 50% of the initial (t 0) readings in Figures 1c and 1d. (iv) The action spectra in Figure 1 show that the dihydrate polymer (Chl $a\cdot 2H_2O)_n$, corresponding to the 740-nm band,[6b] is primarily responsible for the enhancement effects. The 673-nm band (attributable to monohydrate Chl a complexes[6b]), which is approximately equal in importance to the 740-nm band at pH 7 in the absence of divalent cations such as Fe^{2+}, Ba^{2+}, Ca^{2+}, or Zn^{2+} (see Figure 1a and Figure 1A (a) of ref 6b), becomes relatively unimportant upon addition of the low-pH buffers or divalent cations. (v) An increase in the photocurrent is also observed when the pH of the Chl a free half cell is increased (Figure 1e), although the effect is significantly less pronounced than the corresponding effects in i and ii. (vi) The pH effect