table also shows that the increase of acidity by the second introduction of the same group is only some 60% of that by the first. Such attenuation with continued substitution is generally observed in the gas phase.[1-4] When the second substituent is different and more weakly acidifying than the first then the observed attenuation is larger. Thus introducing phenyl into acetylmethane leads to an acidity increase of 13.9 kcal/mol while introducing phenyl into the weaker acid phenylmethane leads to an increase of 19.9 kcal/mol. Similarly introducing phenyl into cyanomethane gives 12.6 kcal/mol which is also small compared to the 19.9 kcal/mol for introducing phenyl into phenylmethane. The introduction of acetyl into benzoylmethane leads to an acidity increase of 21.4 kcal/mol while acetyl into acetylmethane gives 22.1 kcal/mol. The difference in this case is smaller, a result that does not quite fit the trends mentioned above.

It is interesting to compare malononitrile, $(D - EA) = 17.2$ kcal/mol, with the somewhat weaker chloroacetic acid, $(D - EA) = 19.6$ kcal/mol.[6] In aqueous solution malononitrile[17] with a pK_a of 11.2 is drastically weaker than chloroacetic acid whose $pK_a = 2.9$. It follows that the acetate anion must be much more strongly hydrated than the carbanion even though the two anions are of similar size. The hydration difference should be due to two factors. Since carbon is not as electronegative as oxygen, acidity in carbon acids can be achieved only through charge dispersal by means of σ- and π-withdrawing groups. However, charge dispersal leads to low hydration interactions.[18] Secondly the carbanion has only one strong hydrogen bonding position, while the oxygen atom has two. The same two reasons to a greater or lesser degree make all carbon acids relatively much weaker in aqueous solution.

The acidities of the β-dicarbonyl compounds are further complicated by keto enol and tautomerism, steric effects, and dipole–dipole repulsions. The nature of these effects will be discussed in a future publication.[8]

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Complexes of Benzyl Isocyanide with Ferrous Phthalocyanine. A Model for the Heme Group and a Solar Energy Storage System

Sir:

Although extensive studies of thermal and photochemical dissociation of alkyl isocyanides from hemoglobin and myoglobin have been reported,[1-3] studies of the reactions of alkylisocyanides with simple iron complexes which might reasonably serve as models for the heme group have been limited.[4,5] In previous papers we have reported on the kinetics and equilibria of carbon monoxide binding to iron porphyrin and phthalocyanine complexes in toluene solution.[6,7] While the iron porphyrins bind CO by a factor of 10^5 times better than the corresponding iron phthalocyanine complexes (in terms of the equilibrium $L_2FeP + CO = LFeP(CO) + L$ where L = piperidine and P = protoporphyrin IX or phthalocyanine) the lability of the CO in the two systems is comparable and considerably greater than that reported for CO dissociation from iron glyoxime[8] or iron macrocycle systems.[9] In order to fully elucidate those features of the porphyrin ligand which gives rise to the unusual lability of ligands coordinated in axial positions,[10,11] we have extended our investigations to alkyl isocyanide ligands.

We report here on a markedly different lability of benzyl isocyanide (RNC) in the phthalocyanine (Pc) and porphyrin (P) systems and also on a novel photochemical dissociation of benzyl isocyanide which results in a reversible shift in an equilibrium due solely to light and a net storage of solar energy.

Addition of pyridine, piperidine, or methylimidazole to a toluene solution of (dibenzyl isocyanide)ferrous phthalocyanine ($FePc(RNC)_2$),[12] results in a rapid reaction ($k = 0.1$ sec^{-1} at 20°) to give the monoisocyanide complex

$$FePc(RNC)_2 + L = LFePc(RNC) + RNC \quad (1)$$

Further reaction to give the diamine complex

$$LFePc(RNC) + L = L_2FePc \quad (2)$$

is slow in the dark and is markedly dependent on the trans ligand L. Data for L = piperidine, pyridine, or methylimidazole show relative trans effects similar to those previously reported for CO dissociation from the analogous LFePc(CO) complexes (Table I). For each of the ligands, L, the rate of benzyl isocyanide dissociation is a factor of $\sim 10^3$ slower than the corresponding rate for CO. The large differences in RNC and CO lability stem from a similar difference in the stability constants.

Table I. Kinetic Data for Benzylisocyanide and Carbon Monoxide Dissociation from Ferrous Phthalocyanine Complexes in Toluene Solution

L trans	k_{RNC},[a] sec^{-1}	k_{CO},[b] sec^{-1}
Piperidine	5.15×10^{-4}	0.13
Pyridine	1.98×10^{-4}	0.09
Methylimidazole	9.2×10^{-5}	0.02
Hemoglobin[c]	0.2	0.015

[a] This work, 30°. [b] 23°, ref 7. [c] For aqueous solutions, 20°, pH 7; from ref 1 p 276; RNC = ethylisocyanide.

Alkylisocyanides coordinated to hemoglobin or myoglobin or to free iron porphyrins do not display the inertness which is observed in the phthalocyanine sys-

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tem. The rate of dissociation of alkylisocyanides from the proteins is faster than CO dissociation (Table I).

It should be noted that the marked difference in binding of alkylisocyanides to hemoglobin and myoglobin with increasing steric bulk of the alkyl group, R,[13] is due almost entirely to a difference in "on" rate, not to differences in "off" rates.[14] We have made preliminary measurements on the rate of isocyanide dissociation from the free heme complexes by displacement with carbon monoxide according to the reaction

$$\text{LFeP(RNC)} + \text{CO} = \text{LFeP(CO)} + \text{RNC}$$

where L = piperidine and P = protoporphyrin IX. We find the rate of displacement of benzyl isocyanide to be comparable to rates observed for other isocyanides in the protein systems. This result is consistent with our previous report that the protein has little effect on the rate of CO dissociation.[7] It should be noted that in the case of polar molecules bound to the protein such as NO^- or O_2^-, one observes a substantially different rate of dissociation outside of the protein environment[15,16] consistent with the idea that the protein serves to insulate the heme group from solvation effects.[16,17] This effect of solvent on the "off" rates explains the much poorer oxygen binding observed in cobalt[18] and iron model[19] systems compared to the binding in the proteins.

While the dissociation of benzyl isocyanide from ferrous phthalocyanine is slow in the dark, the reaction is rapid in the presence of normal fluorescent room lighting. Over a thousandfold increase in rate is observed between dark and full illumination. The observed increase in the rate of dissociation in the presence of light results in a shift of the equilibrium

$$\text{L}_2\text{FePc} + \text{RNC} = \text{LFePc(RNC)} + \text{L} \qquad (3)$$

The effect is quite dramatic. Solutions containing concentrations of L and RNC to shift the equilibrium to the right appear blue. In the presence of light the color rapidly changes to the green color of L_2FePc. On placing the solution in the dark, the color changes back to blue. The change in color from blue to green and back again has been repeated several hundred times without any loss in reversibility. The relative rate of return to "true equilibrium" in the dark may be varied by changing the ligand L.

Photodissociation of CO and RNC from hemoglobin and myoglobin is well known.[1] A similar effect of light on the equilibrium for CO binding to hemoglobin and myoglobin has recently been reported.[20,21]

We know of no previous suggestion that solar energy storage in biological systems may occur by a process similar to that observed in the iron phthalocyanine model system. The remarkable versatility of such a process and the similarity between the iron phthalocyanine and biological metal complexes make such a proposal very attractive. We are continuing our investigations of the kinetics and equilibria of substitution reactions of iron phthalocyanine and porphyrin complexes with the goal of optimizing energy storage and determining how this stored energy may be used to drive unfavorable reactions in much the same way ATP is used to drive biological reactions.[22]

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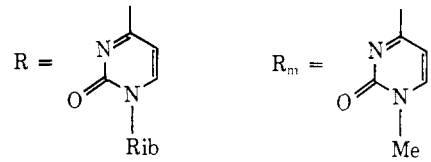
Mechanism of Reduction of 1-Methyl-4-thiocyanatouracil by Bisulfide. A Route to *in Vitro* Labeling of tRNAs with Sulfur-35[1,2]

Sir:

It has been recently demonstrated[3-5] that 4-thiocyanatouridine and its methyl analog undergo nucleophilic C–S bond scission by OH^-, with the formation of the thio and oxo compounds in the ratios 2:7 and 1:1, respectively, according to 1 and 2. The stoichiom-

$$9\text{RSCN} + 18\text{OH}^- = 7\text{RO}^- + 2\text{RS}^- + 7\text{SCN}^- + 2\text{OCN}^- + 9\text{H}_2\text{O} \qquad (1)$$

$$2\text{R}_m\text{SCN} + 4\text{OH}^- = \text{R}_m\text{O}^- + \text{R}_m\text{S}^- + \text{SCN}^- + \text{OCN}^- + 2\text{H}_2\text{O} \qquad (2)$$



etry of the reactions has been established by estimating spectrophotometrically the amounts of RS^-, RO^-, R_mS^-, R_mO^-, and SCN^- formed in these reactions. In the case of reaction 2, the quantitative uptake of alkali has been determined by titration. These results indicate that the pyrimidine ring C–S bond is more vulnerable to nucleophilic attack than the exocyclic C–S bond in RSCN. In a parallel reaction, both RSCN and R_mSCN are reduced quantitatively by the nucleophile SH^-. If this reaction occurs mostly by the pyrimidine ring C–S fission, one should be able to incorporate ^{35}S label in RSH by using $^{35}SH^-$ as a reagent. We have investigated the mechanism of the

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