Solvent Control of Selective Ligand Labilization in Transition Metal Photochemistry

By JEFFREY I. ZINK* and MICHAEL J. INCORVIA

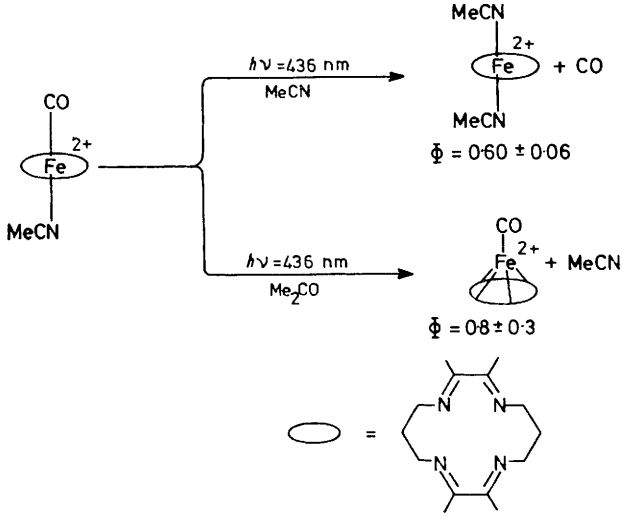
(*Department of Chemistry, University of California, Los Angeles, California,* 90024)

Summary The ligand photolabilization of *trans*-$[Fe(tim)(CO)(MeCN)]^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene) is controlled by the solvent with loss of CO occurring when the complex is photolysed in acetonitrile but loss of acetonitrile occurring when it is photolysed in acetone.

THE most common photoreaction of transition metal complexes is photosolvation.[1] In mixed ligand complexes, the identity of the photolabilized ligand can be explained in terms of the σ- and π-bonding properties of the ligands and the electronic properties of the excited state responsible for the photoreaction.[2] In addition, the relative quantum yields of a series of complexes studied under similar conditions can be explained in terms of bonding and electronic properties.[3] When the fluid medium in which the photoreactions are studied is changed, the quantum yield of a reaction can also be changed. A recent quantitative study demonstrated the effects of viscosity and entering ligand concentration on reaction quantum yields.[4] However, solvent control of the preferential labilization of one ligand over another has heretofore been unknown. We report here, as the first example of solvent control of ligand labilization, selective loss of carbon monoxide or acetonitrile from $[Fe(tim)(CO)(MeCN)]^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene).[5]

The square planar Fe(tim) species form a variety of axially disubstituted complexes.[5] An intense metal d_{xz}-d_{yz}-to-tim charge transfer band is observed in the visible region of the spectrum which moves to higher energy with increasing π-acceptor ability of the axial ligands: $[Fe(tim)(NH_3)_2]^{2+}$, λ_{max} 700 (ϵ 5970 l mol^{-1} cm^{-1}); $[Fe(tim)(imidazole)_2]^{2+}$, 658 ($\epsilon$ 9550); $[Fe(tim)(MeCN)_2]^{2+}$, 550 (ϵ 9870) and 513 (ϵ 5766); $[Fe(tim)\{P(OEt)_3\}_2]^{2+}$, 513 ($\epsilon$ 9200); and $[Fe(tim)CO(MeCN]^{2+}$, 431 (ϵ 6200) nm.

When a 10^{-4}M solution of $[Fe(tim)(CO)(MeCN)]^{2+}$ in acetonitrile at 15 °C is irradiated at 436 nm in the metal-to-tim charge transfer band, the intensity of this band smoothly decreases with a corresponding appearance of new bands at 513 and 550 nm characteristic of the $[Fe(tim)(MeCN)_2]^{2+}$ complex. The presence of an isosbestic point at 463 nm is indicative of a clean photoreaction with negligible side reactions. The reaction and its quantum yield are shown in the Scheme.



SCHEME

When a 10^{-4}M solution of $[Fe(tim)(CO)(MeCN)]^{2+}$ in acetone at 15 °C is irradiated in the metal-to-tim charge transfer band, the intensity of the 431 nm band again smoothly decreases. However, the new band appears at

450 nm and the isosbestic point occurs at 448 nm. The very small red shift of the charge transfer band of the photoproduct indicates that the product contains co-ordinated carbon monoxide. Only the presence of a good π-acceptor like CO would cause the band to appear in the blue region of the spectrum. Also, an i.r. analysis of the photoproduct shows an intense peak at 2020 cm^{-1}, a shift of 8 cm^{-1} to lower energy than that of the photoreactant. The photoproduct is thus either $[Fe(tim)(CO)(acetone)]^{2+}$ or a five-co-ordinate carbonyl complex, $[Fe(tim)CO]^{2+}$. Because the absorption band of the photoproduct overlaps that of the starting material, the calculation of the concentration changes and the quantum yield are accurate to only $\pm 25\%$.

The above results show that the quantum efficiency for CO loss is large ($\phi = 0{\cdot}60$) when the photolysis is carried out in acetonitrile, but very small ($\phi < 10^{-2}$) when it is carried out in acetone. The data do not show whether or not the quantum efficiency for loss of acetonitrile is significant in acetonitrile because the photochemical loss of acetonitrile would produce a photoproduct indistinguishable from the starting material. Attempts to resolve this question by using the substituted nitriles, benzonitrile, trimethylacetonitrile, and propionitrile, have been unsuccessful because of the sensitivity limits of analytical techniques for the detection of nitriles in nitrile solvents and by the thermal lability of the axial ligands. The thermal exchange reactions of the nitriles and CO also severely complicate both labelling and scavenging studies.

The observed solvent control of the ligand labilization can be explained in terms of two mechanisms: associative solvent attack on a six-co-ordinated excited state, or photodissociative production of five-co-ordinate solvent caged intermediates followed by solvation. In the iron-to-tim charge transfer transition the d_{xz} and d_{yz} orbitals are depopulated, formally oxidizing the metal and weakening the metal–ligand π back-bonding. If the activation energy in the excited state for CO displacement is higher than that for acetonitrile displacement, a poor nucleophile might be able to displace acetonitrile but not CO while a good nucleophile would be able to displace both. Alternatively, the primary photoreaction could be dissociative. If co-ordinated acetonitrile were lost in both solvents, acetonitrile but not acetone might be able to displace CO from the five-co-ordinate intermediate. If both CO and MeCN were lost in both solvents, the final product distribution might be governed by the relative rates of the recombination reactions of the solvent caged species compared to those of the scavenging reaction.

We thank the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award to J.I.Z.

(*Received*, 24*th June* 1977; *Com.* 635.)

---

[1] A. W. Adamson and P. O. Fleischauer, 'Concepts of Inorganic Photochemistry,' Wiley, New York, 1975.
[2] J. I. Zink, *J. Amer. Chem. Soc.*, 1972, **94**, 8039; *Inorg. Chem.*, 1973, **12**, 1018.
[3] M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, 1974, **13**, 2489.
[4] P. Liu and J. I. Zink, *J. Amer. Chem. Soc.*, 1977, **99**, 2155.
[5] D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Amer. Chem. Soc.*, 1973, **95**, 5152.