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Preliminary communication

Photochemistry of $Fe(CO)_3[P(p\text{-}C_6H_4CH_3)_3]_2$ and $W(CO)_4[P(i\text{-}C_3H_7)_3]_2$ and the apparently anomalous behaviour of $(cyclo\text{-}C_4H_4)Fe(CO)_3$

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SUMMARY

The behaviour of metal carbonyl phosphines in matrices and in solution strongly suggests that the failure to generate cyclobutadiene from matrix isolated tricarbonylcyclobutadieneiron is due to a cage effect, and exemplifies a general limitation of matrix photochemistry as a test of solution or vapour phase reaction mechanisms.

It has recently been reported that while vapour phase irradiation of tricarbonylcyclobutadieneiron (I) gives free cyclobutadiene[1], irradiation in a krypton matrix at 8K gives at least predominantly dicarbonylcyclobutadieneiron and carbon monoxide[2] (this latter result closely parallels our own observations with tricarbonylcyclopentadienylmanganese[3] in hydrocarbon glasses at 77K). We wish to point out that a similar anomaly arises with other metal carbonyl derivatives, and to suggest an explanation.

We have investigated the photolytic behaviour of a large number of metal carbonyl derivatives, including metal carbonyl phosphine complexes, in inert (isopentane–methylcyclohexane) or in donor (*e.g.* 2-methyltetrahydrofuran) glasses, and in mixtures of these. In all cases the only reactions observed in the matrices are loss of carbon monoxide (with possible isomerisation of unsaturated fragments[4]) and its replacement by donors. We have not observed loss of phosphorus ligands or even of phosphine itself** However, irradiation of bis (tri-*p*-tolylphosphine)tricarbonyliron (II) in hydrocarbon solution under a carbon monoxide atmosphere gives within minutes tri-*p*-tolylphosphinetetracarbonyliron (III) and presumably free ligand. A steady state is eventually established, and the reaction may be reversed by removing carbon monoxide while irradiating. There is no detectable dark reaction over several days, nor does the photochemical reaction produce detectable amounts of pentacarbonyliron. Quantitative IR studies showed the amount of (III) generated to be equal to the amount of (II) lost. No $Fe(CO)_5$ could be detected

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** *Note added in proof* We have now observed some formation of $Mo(CO)_6$ from $Mo(CO)_5PH_3$ in hydrocarbon glass, but confirm that this reaction is not observed for complexes of other phosphine ligands under our conditions.

either in the reaction solution or in a downstream paraffin bubbler. The electronic absorption spectrum of II is broad, featureless, and moderately intense, and it thus seems unlikely that any excited state could persist long enough to take part in a bimolecular reaction. We infer that a primary process in the solution photochemistry of (II) is loss of a phosphorus ligand. Loss of carbon monoxide may of course also be taking place, escaping detection because of recombination; the same is true for the vapour phase photolysis of (I). We do not know whether (III) also shows photochemical loss of phosphine ligand; the failure to form pentacarbonyliron is not significant, since it is known that the reaction of the tetracarbonyliron fragment in solution with tri-*p*-tolylphosphine is faster than its reaction with carbon monoxide[5].

Solubility problems have so far prevented us from investigating the matrix photochemistry of (II). However, both matrix and solution studies have now been carried out on bis(triisopropylphosphine)tetracarbonyltungsten (IV). Here again we find, in solution, photochemical replacement of one phosphine ligand only by free carbon monoxide. Photolysis of (IV) in hydrocarbon or in methyltetrahydrofuran (MeTHF) glasses does not, however, lead to formation of products of the type $LM(CO)_4$ or $LM(CO)_4MeTHF$, although such products may be readily formed starting from species $LM(CO)_5$ [4]. The expected loss of carbon monoxide from (IV) is, however, observed*, but is very much slower than that found in the $LM(CO)_5$ species [4,6].

Our explanation is that, should loss of a phosphine ligand occur in the matrix photolysis of (II) or (IV), the ligand is unable under our conditions to escape from the solvent cage, and the reaction is masked by recombination. This is so even when the matrix material is of a type to react with the fragment which would be formed by such loss. It is now generally agreed that cage effects play a major role in the loss of carbon monoxide from binary carbonyls and in the pseudo-photochemical reversal of this process[7,8]. It follows that matrix isolation photolysis is a poor test of photochemical mechanisms involving the displacement of relatively bulky groups. Whether a soft (solution) cage would suffice to prevent loss of cyclobutadiene from (I), whether reversible carbon monoxide loss from (I) takes place even in the vapour phase, and what the sequence of events may be in the solution photochemistry of (I), remain open questions.

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*Bands at 1838 and 1817 cm^{-1} observed in 4/1 methylcyclohexane/isopentane glass at 77K after 60 min photolysis with unfiltered light from a medium pressure Hg discharge lamp are assigned to $W(CO)_3[P(i\text{-}C_3H_7)_3]_2$. A weak band at 2138 cm^{-1} due to trapped CO is also observed. In MeTHF only trapped CO and one new band at 1825 cm^{-1} were observed after 180 min photolysis.

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