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Preliminary communication

CONTRASTING PHOTOSUBSTITUTION REACTIONS OF DIAZANORBORNENE-CHROMIUM AND -TUNGSTEN PENTACARBONYLS

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Summary

Electronic excitation causes efficient labilization of both the azo and carbonyl ligands in $Cr(CO)_5$(diazanorbornene) via an excited LF state. On the contrary the corresponding tungsten complex undergoes only inefficient azo labilization via a MLCT state. Azo labilization is also promoted by electron-transfer sensitization.

Transition metal carbonyl complexes are usually photolabile. The relative rates of labilization of different ligands and their relation to the structure of the excited state involved are subjects of active interest [1]. We report the unusually clear cut difference in substitutional behaviour between ligand field and internal charge transfer excited states which is observed in the case of C_{4v} complexes $M(CO)_5L$, where L is an azo compound, viz. diazanorbornene (2,3-diazabicyclo-[2.2.1]hept-2-ene), and M = Cr or W (Ia, Ib).

Many metal carbonyl complexes containing *cis*-aliphatic azo derivatives have been described [2], but little is known about their photochemistry. The absorption spectrum of compounds Ia, Ib shows features similar to those of the corresponding pyridine complexes [3]. The tungsten complex absorbs at somewhat shorter wavelength and shows no maximum attributable to the $^1A \rightarrow {}^3E$ transition, which appears only as a weak long wavelength tail.

The main band for both complexes has a relatively high absorption coefficient and shows a strong blue shift in polar solvents. Thus, it arises from superimposition of the $^1A \rightarrow {}^1E$ LF transition and a MLCT transition (cf. ref. 3).

The chromium complex is significantly reactive in solution even at 40°C, while the tungsten complex is much more stable, but in both cases the thermal reaction involves exclusive labilization of the azo ligand. The photochemical reactivity is more varied. Thus, while in "inert" solvents some $M(CO)_4L_2$ is formed, in the presence of virtually any ligand L′ the processes depicted in eq. 1 and 2 are observed in clean reactions.

$$\mathrm{M(CO)_5L} \xrightarrow[\mathrm{L'}]{h\nu} \mathrm{M(CO)_4LL'} \qquad (1)$$

(Ia,Ib) (IIa,IIb)

$$\mathrm{M(CO)_5L} \xrightarrow[\mathrm{L'}]{h\nu \text{ or } \Delta \text{ or Sens}^{3\star}} \mathrm{M(CO)_5L'} \qquad (2)$$

(Ia,Ib) (IIIa,IIIb) ($\mathrm{Sens}^{3\star}$ = triplet sensitizer)

The new complexes II (L′ = triphenylphosphine) were identified from their analyses and spectroscopic properties.

The chromium and tungsten complexes are strikingly different both in the decomposition quantum yield (Φ_{disap}), which is almost two orders of magnitude lower in the latter case, and in the balance between processes 1 and 2, the latter being very minor with Ib (see Table 1). The insensitivity of the reaction to the concentration ($[\mathrm{L'}] \geqslant 10^{-3}$ *M*) to the nature of L′, or to the use of complexating solvents such as MeCN shows that the primary photoprocess is the labilization of a ligand followed by capture of the reactive fragment by L′, as is usually the case in photosubstitution of metal carbonyls. Oxygen has no effect on the reaction.

TABLE 1

REPRESENTATIVE DATA FOR THE SPECTRA AND THE PHOTOREACTIVITY OF COMPLEXES Ia AND Ib[a]

		$\mathrm{Cr(CO)_5L}$ (Ia)		$\mathrm{W(CO)_5L}$ (Ib)	
λ_{max} (nm)	Cyclohexane	398 (8300)		386 (9600)	
(ϵ)	Ethanol	387 (7500)		379 (8800)	
λ_{irr} (nm)		366	434	366	434
Φ_{disap}		0.71	0.6	0.022	0.021
$\Phi_{\mathrm{eq.\ 1}}$		0.4	0.32	0.004	0.001
$\Phi_{\mathrm{eq.\ 2}}$		0.31	0.28	0.018	0.02

[a] Experiments in cyclohexane, L′ = triphenylphosphine

In the case of the chromium complex, flash photolysis reveals an intermediate of similar characteristics to the known $\mathrm{Cr(CO)_5}$(Solvent) complex [5], whereas no detectable transient species ($\tau \geqslant 2\mu$s) is observed in the case of the tungsten complex. Thus the photostability of complex Ib is related to a different excited state situation rather than to a rapid dissociation—recombination process. The inefficiency originates partly in the greater role of intersystem crossing and internal conversion (due to higher density of vibrational levels) in the case of the tungsten complex, and partly in a reversal of the excited state ordering.

Thus, the high quantum yield observed for the chromium complex is in accord with a reaction from a singlet LF state, in which labilization of an equatorial CO group competes with labilization of the axial diazanorbornene group. (For a discussion of a similar case, see ref. 4). The situation may be reversed in the tungsten complex, so that the unreactive MLCT state becomes the lowest excited state. There is no spectroscopic evidence for this changed order (both complexes show practically no emission at 77 K), except in the blue shift of the absorption of Ib compared with Ia, but the difference in the thermally equilibrated excited states involved in photochemistry could escape spectroscopic detection.

To check the role of triplet states, sensitization experiments were carried out. After taking into account the correction for the inner filter effect (cf. ref. 6), it emerged that benzophenone sensitizes exclusively process 2, whereas fluorene, the triplet energy of which is similar, is totally ineffective.

The small amount of evidence for triplet sensitization of metal carbonyls reactions is limited to ketones [6—8], and the inefficiency of hydrocarbon sensitizers has been noticed [6]. Although it was convincingly shown in a related case that ketone sensitization is really due to the quenching of the triplet state and not to chemical initiation by ketyl radicals [6], no satisfactory explanation has been found for the contrasting behaviour of hydrocarbon sensitizers. Thus we understand the sensitization by ketones as due to partial electron transfer rather than to energy transfer (eq. 3):

$$\mathrm{Sens}^{3\bigstar} + \mathrm{M(CO)_5L} \rightarrow [\mathrm{Sens}^{\delta-}\cdots\mathrm{M(CO)_5L}^{\delta+}] \rightarrow \mathrm{Sens} + [\mathrm{M(CO)_5}] + \mathrm{L} \qquad (3)$$

This is supported by the known ability of metal carbonyls to quench excited states by electron transfer [9] and by a recent report which shows the efficiency of ligand substitution in metal carbonyls by anodic catalysis [10]. The situation would then be similar to that in the well known quenching of ketones triplets by amines, which also involves electron transfer [11].

Thus metal oxidation both intramolecularly in the MLCT excited state or intermolecularly leads to exclusive labilization of the azo ligand. The low reactivity of the MLCT state is well understood as due to the poor delocalization possible with the azo ligand in comparison, e.g., to pyridine, which makes back electron transfer the dominant process.

In conclusion, metal carbonyl complexes containing aliphatic azo ligands show a marked difference in chemical behaviour of the LF and MLCT states and this appears to offer a useful tool for understanding the photochemistry of carbonyl complexes.

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