Photochemistry of π-Cyclopentadienylcarbonylmetal Halides in Dimethyl Sulphoxide and Related Solvents

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The principal product when solutions in dimethyl sulphoxide or pyridine of π-cyclopentadienylcarbonylmetal halides of Fe, Mo, and W are irradiated at long wavelengths ($\lambda > 400$ nm) is a dimer: this is $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ in the case of Fe (indicating loss of halogen) but appears to be $[(\pi\text{-}C_5H_5)M(CO)_2Cl]_2$ for Mo and W; free cyclopentadiene and chloride ion are also produced in the case of Fe. The reactions do not proceed in non-polar solvents. At shorter wavelengths ($\lambda > 280$ nm) the principal product in all cases is a dimeric species which could not be isolated, but which spectral data suggest to correspond to displacement of one CO molecule by solvent from the dimers obtained at longer wavelengths; moreover i.r. and n.m.r. spectral profiles of the $\lambda > 280$ nm reaction indicate that the latter are essential intermediates in all three cases.

THE primary process dominating the photochemistry of many metal and arenemetal carbonyls is that of elimination of one molecule of CO to leave an unsaturated intermediate, which rapidly co-ordinates with a solvent molecule S,[1,2] *viz.*

$$ArM(CO)_x \xrightarrow{h\nu} ArM(CO)_{x-1} + CO \qquad (1)$$

$$ArM(CO)_{x-1} + S \longrightarrow ArM(CO)_{x-1}S \qquad (2)$$

unless it is prepared either in an inert matrix,[3-5] in which case it can be rendered sufficiently stable for i.r. and u.v. examination, or in a non-co-ordinating solvent, in which case the end-product corresponds to a disproportionation,[6] *e.g.*

$$6Cr(CO)_5 \longrightarrow 5Cr(CO)_6 + Cr$$

which clearly involves a sequence of several steps. Evidence for the unsaturated intermediates has also been obtained from room-temperature flash photolysis work.[7,8] An alternative type of product is a polynuclear derivative, for example, photolysis of $(\pi\text{-}C_5H_5)Rh(CO)_2$ and $(\pi\text{-}C_5H_5)Co(CO)_2$ [9,10] yields $(\pi\text{-}C_5H_5)_2Rh_2(CO)_3$ and $[(\pi\text{-}C_5H_5)CoCO]_3$ respectively.

We were prompted to investigate the solution photochemistry of molecules of the type $(\pi\text{-}C_5H_5)M(CO)_xX$ where M = Fe, Mo, or W, and X = Cl or Br to determine whether the usual mode of CO elimination yielded a halogen-substituted intermediate or whether the relatively facile photohomolysis[11] of the M–X bond would occur. Replacement of the remaining CO ligands by solvents (S) in the former case would yield an entity of the type $(\pi\text{-}C_5H_5)M(S)_xX$ proposed as an intermediate in the photochemistry of a variety of carbonylferrocenes in solvents such as dimethyl sulphoxide (DMSO), dimethylformamide (DMF), pyridine, and hexamethylphosphoric triamide (HMPT).[12]

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Neither of these expectations was realised in the case of $(\pi\text{-}C_5H_5)Fe(CO)_2X$: while halogen is eliminated with irradiation wavelengths >400 nm, this occurs only in the solvents active in carbonylferrocene photochemistry, *i.e.* DMSO, DMF, and HMPT, and the main products are dimers which undergo a secondary photosolvolysis reaction when a terminal CO group is replaced.

EXPERIMENTAL

Our general techniques of irradiation and monitoring of reactions have been described fully.[12] Materials were prepared by standard procedures and purified by column chromatography and recrystallisation.

RESULTS

π-Cyclopentadienylcarbonyliron Halides.—Irradiation of 2 mM $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ (I) in DMSO ($\lambda > 280$ nm) resulted in a rapid and systematic increase in absorption over the whole u.v. range although the characteristic peaks of (I) at 392 and 336 nm gave way to a structureless absorption (no dark reaction was detectable over a period of 1 month). By confining the irradiation to $\lambda > 400$ nm, an isosbestic point was apparent with a 800 μM solution of (I) in DMSO at $\lambda = 385$ nm with the decrease in absorption at $\lambda >$ 385 nm and with $\lambda_{max.}$ *ca.* 336 nm, indicating a smooth transformation of the type $A \longrightarrow B$ at $\lambda > 400$ nm but a more complex process at $\lambda > 280$ nm. *In situ* irradiations of (I) in pyridine or DMSO in an i.r. cell (NaCl windows) indicated a similar dichotomy; irradiation ($\lambda > 280$ nm) of pyridine solutions of (I) (180 mM) and $(\pi\text{-}C_5H_5)Fe(CO)_2Br$ (270 mM) initially resulted in the gradual removal of the i.r. absorptions of the former (2045, 1990 cm^{-1}) and of the latter (2043, 1993 cm^{-1}) with the simultaneous formation of peaks at 1984s, 1945m, 1776s cm^{-1} identical in each case. When *ca.* 30% of the halide had disappeared, the build-up of the 1776 cm^{-1} absorption slowed and new peaks at 1930m and 1723s cm^{-1} began to emerge, which grew at the expense of the 1776 cm^{-1} peak (even after the halide had completely photodecomposed) until the latter itself vanished, suggestive of a sequence $A \longrightarrow B \longrightarrow C$. The first step in this sequence could be isolated by insertion of a filter (Corning GR3) transmitting beyond 400 nm when (I) (180 mM) in pyridine photoconverted to the 1776 cm^{-1} compound but no further. Essentially identical changes were found using λ(irradiation) > 280 nm with solutions of (I) in $[^2H_6]$DMSO in which the $\pi\text{-}C_5H_5$ frequency at 3076 cm^{-1} of (I) disappeared together with its carbonyl frequencies (2038, 1983 cm^{-1}) to give the intermediate [1978s, 1938m, 1768s cm^{-1}] and the final product [1952m, 1737s cm^{-1}].

The proton n.m.r. profile also demonstrated the sequential nature of reaction with λ(irradiation) > 280 nm; irradiation of (I) (300 mM) in $[^2H_6]$DMSO over a period of 3 h showed a gradual loss of (I) (τ 4·63) and a build-up of absorptions firstly at τ 5·03 (intermediate) and then 5·90 (final product); additionally new bands appeared at 3·6 and 7·2 with an intensity ratio of 2 : 1 attributable to free cyclopentadiene.

The various spectroscopic data (particularly $\nu_{max.}$) suggest that the intermediate is a bridged carbonyl compound and accordingly experiments were conducted with π-cyclopentadienyldicarbonyliron dimer $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (II) which has $\nu_{max.}$ 1776 (pyridine) and 1768 cm^{-1} (DMSO). With λ(irradiation) > 280 nm, (II) underwent identical u.v., i.r., and n.m.r. changes as found with solutions of (I), and the intermediacy of (II) was confirmed by its successful isolation (140 mg) from the $\lambda > 400$ nm irradiation of (I) (180 mM) in pyridine (380 mg) to the complete destruction of (I) (registered by i.r. spectroscopy) followed by chromatography on silica gel (eluant benzene), as a red crystalline solid, m.p. 190 °C, with i.r., n.m.r., and mass spectra[13] identical to those of authentic dimer.

The remaining member of the photoreaction sequence also displays a bridging carbonyl group i.r. frequency at 1737 and a terminal CO frequency at 1952 cm^{-1} [albeit approximately halved in relative intensity compared with that in (II)], and also n.m.r. absorptions at τ 5·90(s) with weaker multiplets at 1·2—2·8 (both in $[^2H_6]$DMSO) and at 5·6(s), 5·3(s), 2·8(m), 2·3(m), and 1·2(s) in $[^2H_5]$pyridine with approximate integrated intensity ratios of τ(5·6) : τ(5·3) : τ(2·8 + 2·3 + 1·2) of 1 : 1 : 1. The final product (III) was isolated as a dark greenish brown material following irradiation ($\lambda > 280$ nm) of both (I) and (II) in pyridine followed by removal of solvent by pumping. The residue had identical i.r. and n.m.r. spectra in $[^2H_6]$DMSO to the photoproduct in this solvent before its isolation, although the initial i.r. spectrum (1935, 1723 cm^{-1}) changed to that typical in $[^2H_6]$DMSO (1955, 1737 cm^{-1}) over 1·5 h. Its mass spectrum was complicated by the presence of some very high mass number ions, *viz. m/e* values (intensities in parentheses) of 596(1); 419(1); 354(80); 326(30) $[(C_5H_5)_2Fe_2(CO)_3]$; 298(60) $[(C_5H_5)_2Fe_2(CO)_2]$; 270(22) $[(C_5H_5)_2Fe_2CO]$; 242(140) $[(C_5H_5)_2Fe_2]$; 200(29) $[(C_5H_5)FeC_5H_5N]$; 187(180); 186 (v. intense) $[(C_5H_5)_2Fe]$; 184(100); 177(44) $[(C_5H_5)Fe(CO)_2]$; 169(46); 166(35); 149(28) $[(C_5H_5)FeCO]$; 121(430); 95(30); 93(36); 85(100); 84 (most intense) (FeCO); 79(38) (C_5H_5N); 66(230); 65(90), 56(560); 44(120); 28 (v. intense). Although many of these peaks are also given by (II), those at 200, 84, and 79 are not and those in common are in a different intensity ratio. (III) Is very sensitive to heat and it was completely decomposed in solution on bubbling O_2 for 2 min.

Marked evolution of gas was noticed on irradiation of (I) and a sample was analysed mass spectrometrically for Cl_2 but none was detectable at sensitivities of 100 p.p.m. High resolution i.r. examination of the evolved gas showed it to be carbon monoxide.

Irradiation ($\lambda > 400$ nm) of 85 mM (I) in pyridine (2 h), followed by removal of solvent and extraction with benzene left a residue which was extracted with water and filtered. To the filtrate was added excess of 12·5 mM aqueous $AgNO_3$ and the Ag^+ was back-titrated with KCNS solution: 76% of original Cl in (I) was recovered as Cl^-. Fe^{III} was also confirmed by a spot-test.

The solvent dependence of the photoreaction of (I) was examined: in contradistinction to the photoreaction of benzoylferrocene in DMSO and pyridine,[12] reaction proceeded as effectively in rigorously dried media as with (moist) reagent grade solvents. Rapid photodecomposition of (I) took place in tetrahydrothiophen 1-oxide and dimethylformamide to give (II), but in hexamethylphosphoric triamide and acetonitrile neither (II) nor (III) were found and quite different reaction pathways prevail, which are currently under investigation. (I) Was unchanged after photolysis in cyclohexane and diethyl ether for comparable times.

The stoicheiometry of the photoreaction (I) $\longrightarrow$ (II) was measured *in situ* by following the i.r. transformation described above and calibrating the i.r. absorbances of reactant and product using pure materials. Over a con-

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centration range of (I) of 38·6—73·5 mM, (II) was produced in an average molar percentage yield of 21%.

Addition of the free radical scavengers, hydroquinone, and galvinoxyl to the reaction medium was quite without effect on the rate of course of photoreaction, which also failed to induce the polymerisation of styrene (we thank Dr. J. R. Knight for assistance with the latter experiment).

$\phi(-\text{I})$ In DMSO was found to be 0·15 with λ (irradiation) 435 ± 20 nm (isolated with a Balzer filter).

π-Cyclopentadienyltricarbonylmolybdenum and π-Cyclopentadienyltricarbonyltungsten Chlorides.—Irradiation ($\lambda >$ 400 nm) of 800 μM (π-C$_5$H$_5$)Mo(CO)$_3$Cl (IV) in pyridine resulted in the gradual removal of its principal absorption band ($\lambda_{\text{max.}}$ 470 nm) and an increase of absorption in the near u.v. New bands appeared at 560 nm and 400 nm (sh). I.r. studies involving *in situ* irradiation of 100 mM solutions in pyridine revealed, as in the case of the analogous iron compound, a wavelength-dependence of reaction: λ (irradiation) >400 nm resulted in loss of (IV) ($\nu_{\text{max.}}$ 2047, 1960 cm^{-1}) and a build-up of new sharp bands at 1955 and 1858 cm^{-1} (and traces of peaks at 1892 and 1778 cm^{-1}), but with light of higher energy ($\lambda >$ 280 nm) all four of these bands were well developed at the same time. The 1955, 1858 cm^{-1} peaks are associated with a single compound (V) as are those at 1892, 1778 cm^{-1} (VI). Compound (VI) was found to be readily decomposed on exposure to further light, O$_2$ or on being maintained at 40 °C. Compound (V) was far more stable, *e.g.* for one month at room temperature under N$_2$ or for a shorter period in air.

Isolation of (V).—Irradiation ($\lambda >$400 nm) of 100 mM (IV) in deoxygenated pyridine until (IV) had been removed (16 h) followed by pumping away of the solvent (48 h) left a red crystalline residue with i.r. 1962, 1865, 1822 cm^{-1} (Nujol); n.m.r. ([^{2}H$_6$]DMSO) τ 4·2(s). The mass spectrum was highly complex (due to the several isotopic forms of Mo in significant abundance) and the figures refer to those fragments containing ^{96}Mo (figures in parentheses denote relative abundance): 506(1), 470(19), 450(4), 434(22), 422(6), 406(8), 394(30), 378(5), 358(11), 350(3), 329(8), 322(100), 293(11), 257(30), 253(8), 228(86), 226(72), 225(58), 218(17), 197(98), 192(95), 189(14), 161(53), 96(33), 65(56), 36(167).

Chromatography of (V).—Attempted chromatography of the red crystalline residue containing mostly (V) on a silica gel t.l.c. plate (eluant benzene) yielded 3 components with R_{F} values of 0·80, 0·70, and 0·44. On a 30 × 3 cm column (same eluant) it was possible to elute the two high R_{F} components whilst the R_{F} 0·44 component remained for some hours without movement after which it decomposed to release further quantities of the other two components.

Identification of Component with R_{F} 0·80.—This is a dark red crystalline material decomposing at 212 °C with the following spectra; i.r. (pyridine) 1954, 1905 cm^{-1}; n.m.r. [^{2}H$_6$]DMSO τ 4·5(s); u.v. (benzene) $\lambda_{\text{max.}}$ 512, 389 nm; mass spectrum (^{96}Mo isotope) m/e = 490(3), 462(5), 434(9), 406(4), 378(40), 350(1), 322(100), 245(14), 226(4), 217(40), 192(19), 189(22), 161(50), 96(31), 65(19), *i.e.* it is [(π-C$_5$H$_5$)Mo(CO)$_3$]$_2$.

Identification of Component with R_{F} 0·70.—This is a red crystalline material decomposing at 140 °C with i.r. (pyridine) 2047 (s, sharp), 1960 (s, broad) cm^{-1}, n.m.r. [^{2}H$_6$]DMSO τ 4·2(s), u.v. $\lambda_{\text{max.}}$ 470 nm (sh. 320 nm), *i.e.* in all respects it is identical with starting material (IV), (π-C$_5$H$_5$)Mo(CO)$_3$Cl.

The implication of the above observations that (V) decomposes in benzene to give two products, one of which is (IV), was confirmed by i.r. monitoring of a solution of (V) in benzene: the absorptions of (V) at 1960, 1870 cm^{-1} were destroyed and new peaks of (IV) at 2058, 1977 cm^{-1} appeared, the process being completed in 15 min.

Photolysis of (π-C$_5$H$_5$)W(CO)$_3$Cl (VII).—The u.v. and i.r. changes reproduced the behaviour of the Mo analogue. Irradiation of 500 μM (VII) in pyridine resulted in the loss of bands at 458, 320 nm and formation of new bands at 530, 350 nm. With $\lambda >$ 400 nm, the i.r. bands of VII at 2042, 1950 cm^{-1} gave way to principal bands at 1940, 1839 cm^{-1} and minor bands at 1887, 1764 cm^{-1}, but shorter wavelength light resulted in a relative intensification of the latter.

DISCUSSION

Iron Compounds.—The spectroscopic data clearly indicate the photodecomposition of (π-C$_5$H$_5$)Fe(CO)$_2$Cl (I) in DMSO or pyridine to be sequential with λ (irradiation) > 280 nm and to display solvent- and photo-selectivity, *viz.*

$$(\text{I}) \xrightarrow[\substack{\text{C}_5\text{H}_5\text{N or DMSO} \\ \phi\ ca.\ 0{\cdot}15}]{\lambda\, >\, 400\ \text{nm}} (\text{II}) \xrightarrow[\text{C}_5\text{H}_5\text{N or DMSO}]{\lambda\, >\, 280\ \text{nm}} (\text{III})$$

$\lambda_{\text{max.}}$ (nm)	392, 336	*ca.* 336	
$\nu_{\text{max.}}$ (cm^{-1})	2045, 1990	1984, 1945, 1776	1930, 1723
τ [^{2}H$_6$]DMSO)	4·63	5·03 (plus 3·6, 7·3)	5·90

(Spectroscopic data refer to pyridine unless indicated otherwise)

As indicated in the Experimental section, (II) is assigned to [(π-C$_5$H$_5$)Fe(CO)$_2$]$_2$ by comparison with spectra of authentic material. $\nu_{\text{max.}}$ of (III) also indicates a dimeric structure and the shifts of both carbonyl peaks and intensity change of the terminal carbonyl peak, and the slow changes in $\nu_{\text{max.}}$ following dissolution of (III) isolated from pyridine in [^{2}H$_6$]DMSO strongly suggest a photosubstitution of a terminal carbonyl group by pyridine to give (π-C$_5$H$_5$)(CO)Fe(CO)$_2$Fe(C$_5$H$_5$N)(π-C$_5$H$_5$).

The stoicheiometry is exactly half that of 0·5 resulting from a process of the type

$$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl} \longrightarrow (\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2 + \tfrac{1}{2}\text{Cl}_2 \qquad (1)$$

$$(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2 \longrightarrow \tfrac{1}{2}[(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2 \qquad (2)$$

and such a process is ruled out by the absence of Cl$_2$ in evolved gases and the failure of the irradiated mixture to induce polymerisation. There is no reason, again, why (1) should be confined to solvents like DMSO and fail to proceed in cyclohexane or diethyl ether. Rather, the effectiveness of basic, co-ordinating solvents of medium or high dielectric suggests a new mode of reaction in this series of compounds, *i.e.* a heterolysis to give a cationic centre which oxidises (I) to give the necessary oxidation balance between production of Cl$^-$ and formation of dimer, *viz.*

$$(\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{II}}(\text{CO})_2\text{Cl} \xrightarrow[\text{DMSO}]{h\nu} (\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{II}}(\text{CO})_2{}^{+} + \text{Cl}^{-} \qquad (3)$$

$$(\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{II}}(\text{CO})_2{}^{+} + (\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Cl} \longrightarrow (\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{I}}(\text{CO})_2 + (\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{III}}(\text{CO})_2\text{Cl}^{+} \qquad (4)$$

$$(\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{I}}(\text{CO})_2 \longrightarrow \tfrac{1}{2}[(\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{I}}(\text{CO})_2]_2 \qquad (5)$$

$$(\pi\text{-C}_5\text{H}_5)\text{Fe}^{\text{III}}(\text{CO})_2\text{Cl}^{+} \xrightarrow{\text{H}^{+}} \tfrac{1}{2}[\text{C}_5\text{H}_6]_2 + 2\text{CO} + \text{FeCl}^{2+} \qquad (6)$$

Reactions (3)—(6) produce essentially the correct stoicheiometry for dimer and chloride ion and are compatible with the observed production of free cyclopentadiene (detected by n.m.r.), Fe^{III}, and carbon monoxide. While photoheterolyses are rare, they have been authenticated [14,15] for compounds combining electron-rich centres (such as 3-methoxybenzyl) and good leaving groups [$-OAc$, $-OP(OR)_2$] such as we have in the present case.

Molybdenum and Tungsten Compounds.—The i.r. changes indicate reaction sequences of the type

$$\underset{\text{(IV)}}{(\pi\text{-}C_5H_5)Mo(CO)_3Cl} \xrightarrow[\lambda > 400\text{ nm}]{C_5H_5N} \text{(V)} \xrightarrow[\lambda > 280\text{ nm}]{C_5H_5N} \text{(VI)}$$

$\lambda_{max.}$ (nm)	470	560, 400	560, 400
$\nu_{max.}$ (cm^{-1})	2047, 1960	1955, 1858	1892, 1778
τ	4·02 ([$^2H_6$]DMSO)	4·2(s)([$^2H_6$]DMSO)	

$$\underset{\text{(VIII)}}{(\pi\text{-}C_5H_5)W(CO)_3Cl} \xrightarrow[\lambda > 400\text{ nm}]{C_5H_5N} \text{(VIII)} \xrightarrow[\lambda > 280\text{ nm}]{C_5H_5N} \text{(IX)}$$

$\lambda_{max.}$ (nm)	458, 320	530, 350	530, 350
$\nu_{max.}$ (cm^{-1})	2042, 1950	1940, 1839	1887,1764

(Spectral data refer to pyridine solution unless indicated otherwise)

Compound (V) was isolated as relatively unstable dark red crystals ($\lambda_{max.}$ 500 nm, sh. 400 nm in pyridine). Its highest *m/e* peak (506) suggests the parent ion to be $[(\pi\text{-}C_5H_5)Mo(CO)_2Cl]_2^+$ *i.e.* a dimer in which Cl is retained following irradiation in contrast to the Fe analogue; successive loss of Cl atoms produces the peaks at 470 and 434. The fragment at *m/e* 192 is typical of dimeric molybdenum carbonyls [15] and other peaks may be assigned (for the ^{96}isotopic form) to $(C_5H_5)_2Mo_2(CO)_2Cl_2$ (450), $(C_5H_5)_2Mo_2COCl_2$ (422), $(C_5H_5)_2Mo_2Cl_2$ (394), $(C_5H_5)_2Mo_2Cl$ (358), $(C_5H_5)Mo_2Cl_2$ (329), $(C_5H_5)_2Mo_2$ (322), $(C_5H_5)Mo_2Cl$ (293), Mo_2Cl (228), $(C_5H_5)MoCOCl$ (225), $(C_5H_5)MoCl$ (197).

It seems probable that the higher energy photoproduct, by analogy with the Fe dimer (II), might correspond to a solvation product. The lowering of ν(C=O) suggests such a photosubstitution of CO by solvent ligand to give $(\pi\text{-}C_5H_5)(CO)_2MoCl\text{-}ClMo(CO)(C_5H_5N)(\pi\text{-}C_5H_5)$.

The remaining problem concerns the thermal decomposition of (V) in benzene to give (IV) and another product (R_F 0·80). The spectroscopic properties of the latter are completely consistent with those of authentic $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ indicating thermal disproportionation of (V).

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