Evidence for the Formation of the Triaquatricarbonylmanganese(I) Cation and Related Derivatives from Pentacarbonylchloromanganese

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Ready ligand-exchange reactions between water and $[Mn(CO)_5Cl]$ in non-aqueous solution are described. Evidence of various kinds, stoicheiometric, spectroscopic, and electrochemical, is presented which is consistent with the formation under these conditions of aqueous solutions of $[Mn(CO)_3(OH_2)_3]Cl$ (1) which appears to be the first example of this type of complex. The derivative could not be isolated by evaporation of water from the aqueous solution at room temperature since this resulted in decomposition. The ionic equilibria in aqueous solutions of (1) are described, particularly in relation to conductivity and electrolytic data. Photolysis of (1) is believed to lead to protonation and subsequent decomposition with generation of formyl radicals. When benzene solutions of $[Mn(CO)_5Cl]$ are treated with low concentrations (up to 2.5×10^{-2} mol dm^{-3}) of water, non-ionic species of intermediate type appear to be formed, notably $[Mn(CO)_4(OH_2)Cl]$, $[\{Mn(CO)_3(OH_2)Cl\}_2]$, and $[Mn(CO)_3(OH_2)_2Cl]$.

In an earlier paper [1] we studied the reactions of manganese pentacarbonyl halides in non-aqueous solution and demonstrated the ready interconversion of monomeric and dimeric species and derivatives produced by ligand exchange with CO and electron donors. We now report studies of ligand-exchange reactions between $[Mn(CO)_5Cl]$ and water at room temperature; we present evidence that such processes, which are also ready, lead to the

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[1] C. H. Bamford, J. Burley, and M. Coldbeck, *J.C.S. Dalton*, 1972, 1846.

formation of ionic aquacarbonyl species of types which hitherto have not been characterised.

Hieber and Schropp [2] described the formation of ionic complexes of the type $[Mn(CO)_4A_2]Br$ (A = an amine or dimethyl sulphoxide). Very recently, Edwards and Marshalsea [3] prepared a series of cationic complexes of the type $[Mn(CO)_3L_3][ClO_4]$. Hieber and Stanner [4] reported the formation of non-ionic aqua-complexes by reaction (1) (X = Br or I) which was carried out heterogeneously in benzene at 50 °C.

$$[Mn(CO)_3(SPh_2)_2X] + 2H_2O \rightleftharpoons [Mn(CO)_3(OH_2)_2X] + 2SPh_2 \quad (1)$$

Treatment of $[Mn(CO)_3(OH_2)_2I]$ with an aqueous solution (20%) of hydrogencarbonate for 20 h yielded the complex $[Mn(CO)_3(OH_2)_2(OH)]$, which is 'readily soluble in common organic solvents, but only slightly soluble in pentane and water. It is definitely non-ionic'.[4] The related non-ionic rhenium complex $[Re(CO)_3(OH_2)_2Cl]$ has also been described.[5]

EXPERIMENTAL

The complex $[Mn(CO)_5Cl]$ was prepared and purified as described by Abel and Wilkinson.[6] Benzene was dried over sodium wire and distilled *in vacuo* immediately before use. Carbon monoxide (Matheson Co. Ltd.) was obtained from cylinders and used without further purification.

The apparatus employed for spectroscopic and photochemical studies has been described previously.[1,7] Infrared spectra were recorded on a Unicam SP 200 spectrophotometer. The evolution of CO was measured with the aid of a Toepler pump as described previously.[1] Conductivity measurements were carried out with a Griffin and George conductivity cell (cell constant 1.65 cm^{-1}) equipped with bright platinum electrodes (*ca.* 1 × 1 cm). Electrolysis was performed in a cell of total volume 30 cm^3 with two bright platinum electrodes (each *ca.* 1 × 1 cm, 7.5 cm apart).

RESULTS AND DISCUSSION

Reaction between $[Mn(CO)_5Cl]$ *and Water.*—When a solution of $[Mn(CO)_5Cl]$ (5×10^{-4} mol dm^{-3}) in benzene or cyclohexane is shaken with an equal volume of water the yellow colour disappears from the hydrocarbon solution and is transferred to the aqueous phase (Figure 1). The latter has $\lambda_{max.} = 385$ nm and the corresponding absorption coefficient of the new complex (assuming complete conversion) is $\varepsilon_{max.} = 1\,500$ dm^3 mol^{-1} cm^{-1}; $\lambda_{max.}$ is situated in the spectral region encountered with other monomeric manganese(I) carbonyl species which also have similar absorption coefficients. At shorter wavelengths there is a strong band with $\lambda_{max.} = 230$ nm and $\varepsilon_{max.} = 5\,765$ dm^3 mol^{-1} cm^{-1}. The final system is completely unaffected by standing in the presence of 1 atm of CO.*

The results of some measurements of carbon monoxide evolution are presented in the Table. Within the limits of experimental error, it appears that two molecules of CO are evolved for each $[Mn(CO)_5Cl]$ reacting.

Evolution of CO in the reaction between $[Mn(CO)_5Cl]$ and water at 25 °C in benzene or cyclohexane solution (5 cm^3), water (25 cm^3) being added

	10^5 Amount/mol		
Solvent	$[Mn(CO)_5Cl]$	CO evolved	CO/$[Mn(CO)_5Cl]$
Benzene	5.1	9.95	1.95
Cyclohexane	5.2	11.7	1.89
Cyclohexane	3.5	7.66	2.16

The aqueous solution is stable for several days at room temperature in inactive (sodium) light, but attempts to remove excess of water by evaporation *in vacuo* resulted in decomposition (see below). On addition of silver(I) nitrate to the aqueous solution the yellow colour is destroyed, a white precipitate of silver(I) chloride being formed immediately with some reduction to metallic silver. The pH of the aqueous solution remains at *ca.* 7 (see below).

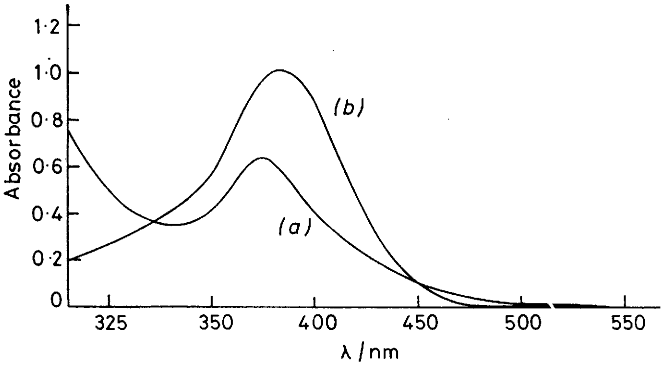

FIGURE 1 Formation of the aqua-complex. Absorption spectra: (*a*) $[Mn(CO)_5Cl]$ (10^{-3} mol dm^{-3}) in dry benzene; and (*b*) aqueous solution of the aqua-complex obtained by shaking (*a*) (5 cm^3) with deionised water (5 cm^3) for 30 min at room temperature. Path length = 10 mm

The simplest explanation consistent with the above findings is the formation of an ionic manganese(I) carbonyl chloride. Cationic manganese(I) carbonyl species are known and well characterised; [2,8] they are always six-co-ordinate (in accordance with the 18-electron rule). We propose that an ionic manganese aquacarbonyl with structure (1) is formed according to reaction (2). Subsequently we shall refer to the derivative(s) formed in aqueous solution as described above as the 'aqua-complex'.

$$[Mn(CO)_5Cl] + 3H_2O \longrightarrow [Mn(CO)_3(OH_2)_3]^+Cl^- \quad (2)$$

It is recognised that substitution of manganese pentacarbonyl halides by donor ligands in general proceeds in accordance with the *trans* effect [6] so that the three molecules of water in (1)

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* Throughout this paper: 1 atm = 101 325 Pa; 1 Faraday ≈ 9.65×10^4 C mol^{-1}.

[2] W. Hieber and W. Schropp, *Z. Naturforsch.*, 1959, **B14**, 460.

[3] D. A. Edwards and J. Marshalsea, *J. Organometallic Chem.*, 1977, **131**, 73.

[4] W. Hieber and F. Stanner, *Chem. Ber.*, 1969, **102**, 2930.

[5] H. Hieber and W. Rohm, *Angew. Chem. Internat. Edn.*, 1968, **7**, 627.

[6] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

[7] C. H. Bamford and C. A. Finch, *Proc. Roy. Soc.*, 1962, **A268**, 553.

[8] E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 117.

would preferentially occupy sites *trans* to the three CO molecules.

Attempts to precipitate the cation from aqueous solutions by addition of solutions containing bulky anions, *e.g.* $[BF_4]^-$, I^-, $[ClO_4]^-$, $[CO_3]^{2-}$, or $[UO_2(O_2CMe)_3]^{2-}$, were unsuccessful. This is probably attributable to the low concentrations of (1) ($<10^{-2}$ mol dm^{-3}) attainable.

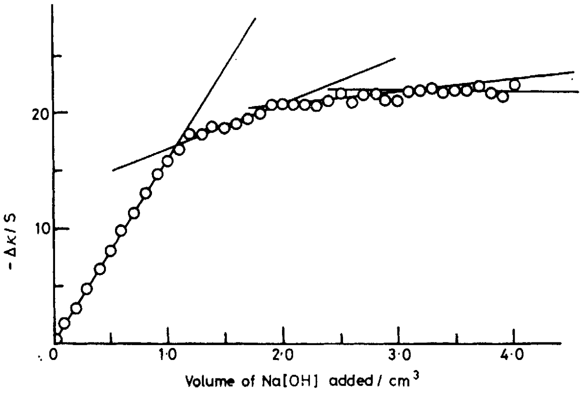

FIGURE 2 Conductimetric titration of an aqueous solution (10 cm^3) of the aqua-complex (1.0×10^{-3} mol dm^{-3}) with Na[OH] (1.09×10^{-2} mol dm^{-3} at 25 °C). Cell constant 1.6 cm^{-1}. $\Delta\kappa$ = (observed conductance) − (conductance expected in the absence of neutralisation). Both conductances are corrected to constant volume

Conductivity Measurements.—A solution of $[Mn(CO)_5Cl]$ in benzene (100 cm^3, 10^{-3} mol dm^{-3}) was shaken with successive portions (10 cm^3) of deionised water until the benzene layer showed no absorption in the visible range. The aqueous washings were collected and made up to 100 cm^3 with deionised water (solution A). The conductivity of solution A was measured at 25 °C and the molar conductance calculated with respect to the $[Mn(CO)_5Cl]$ starting material. It was found to be 124 ± 3 S cm^2 mol^{-1} at 25 °C, in the range normally found for the equivalent conductance λ of strong electrolytes under similar conditions [*e.g.* $\lambda = 127$ S cm^2 mol^{-1} for aqueous NaCl (10^{-3} mol dm^{-3}) at 25 °C]. The pH of the aqueous solution is *ca.* 6.6, so that the contributions to the conductivity arising from H^+ and $[OH]^-$ are negligible. Thus we conclude that 1 mol of $[Mn(CO)_5Cl]$ gives rise to 1 equivalent of electrolyte, consistent with equation (2).

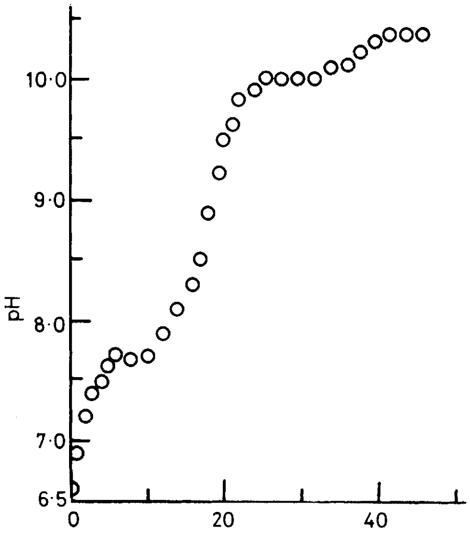

FIGURE 3 Titration of an aqueous solution (15 cm^3) of the aqua-complex (1.02×10^{-3} mol dm^{-3}) against Na[OH] (1.0×10^{-3} mol dm^{-3})

When solution A is titrated conductimetrically against 0.01N Na[OH] the results shown in Figure 2 are obtained. The plot shows a marked discontinuity when 1 equivalent of Na[OH] has been added and a less definite discontinuity when 2 equivalents have been added. There is probably a third discontinuity corresponding to 3 equivalents of Na[OH] but the change hardly exceeds experimental error.

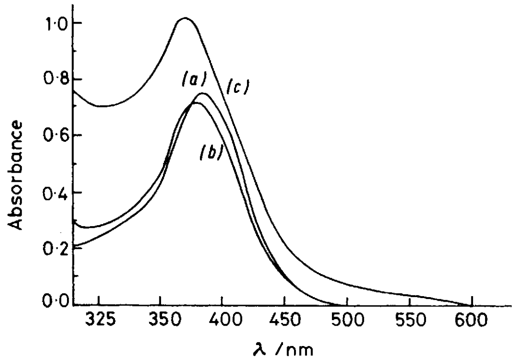

FIGURE 4 Effect of pH on the absorption spectrum of the aqua-complex (5×10^{-4} mol dm^{-3}): (*a*) in distilled water; (*b*) and (*c*) in sodium hydroxide solution (5.0×10^{-4} and 5.0×10^{-2} mol dm^{-3} respectively). Path length = 10 mm

The results are compatible with the reactions (3)—(5). Process (3) leaves the total number of ions in the

$$[Mn(CO)_3(OH_2)_3]^+ + [OH]^- \rightleftharpoons [Mn(CO)_3(OH_2)_2(OH)] + H_2O \quad (3)$$

$$[Mn(CO)_3(OH_2)_2(OH)] + [OH]^- \rightleftharpoons [Mn(CO)_3(OH_2)(OH)_2]^- + H_2O \quad (4)$$

$$[Mn(CO)_3(OH_2)(OH)_2]^- + [OH]^- \rightleftharpoons [Mn(CO)_3(OH)_3]^{2-} + H_2O \quad (5)$$

solution (including Na^+ and Cl^-) unchanged, while (4) and (5) both lead to an increase in the electrolyte concentration of 1 equivalent per equivalent of Na[OH] added. Clearly, addition of Na[OH] gives the same result in the absence of neutralisation. Hence the first discontinuity is very pronounced since from this point onwards the number of ions increases. The other discontinuities arise solely from changes in ionic mobilities and so are much less marked. Similar conclusions may be drawn from pH observations during titration (see Figure 3).

Spectral changes occur on the addition of sodium hydroxide to an aqueous solution of the aqua-complex as indicated in Figure 4. Values of $\lambda_{max.}$ for curves (*b*) and (*c*) occur at 379 and 327nm, respectively, the cor responding values of $\varepsilon_{\mathrm{max.}}$ being 1 410 and 2 040 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$. The observation that $\varepsilon_{\mathrm{max.}}$ for curve (*b*) does not lie between $\varepsilon_{\mathrm{max.}}$ for (*a*) and (*c*) indicates that the species concerned is not a mixture of the absorbing species in (*a*) and (*c*). At shorter wavelengths a shoulder at *ca.* 260 nm appears on addition of Na[OH] while the strong band at 230 nm is little affected.

It should be noted that the non-ionic complex formed by reaction (3) is the same as that prepared by Hieber and Stanner,[4] who, unfortunately, did not report its u.v.–visible spectrum.

We found that when the most concentrated solutions of (1) we could prepare (*ca.* 10^{-2} mol $\mathrm{dm^{-3}}$) were mixed with 1 equivalent of Na[OH] a yellow-brown precipitate appeared. This dissolved in excess of Na[OH]. The precipitate presumably consisted of $[\mathrm{Mn(CO)_3(OH_2)_2(OH)}]$ which Hieber and Stanner [4] report to be insoluble in water. There was insufficient of the material to permit i.r. examination.

From $[\mathrm{Mn(CO)_3(OH_2)_2(OH)}]$ it should be possible to prepare (1) and also the other ionic species in equations (4) and (5). Synthesis of $[\mathrm{Mn(CO)_3(OH_2)_2(OH)}]$ therefore appeared desirable. However, we were unable to repeat the preparation described by Hieber and Stanner [4] starting from either $[\mathrm{Mn(CO)_5Br}]$ or $[\mathrm{Mn(CO)_5I}]$. All the reasonable modifications involving changes in reaction time, temperature, and solvent were tried without success.

Electrolysis.—When a current of *ca.* 100 μA is passed through an aqueous solution of the aqua-complex (10^{-3} mol $\mathrm{dm^{-3}}$) the yellow colour of the complex is discharged rapidly at first but more slowly later. During electrolysis the solution becomes more acidic (final pH *ca.* 4), gas is evolved at both electrodes, and a red-brown solid is deposited on the anode. After passing a total charge of *ca.* 2×10^{-3} Faraday $\mathrm{dm^{-3}}$ (current = 60 μA) the solution contained a concentration of aqua-complex of 0.3×10^{-3} mol $\mathrm{dm^{-3}}$ and 0.2×10^{-3} equivalent $\mathrm{dm^{-3}}$ of acid (determined by conductimetric titration with Na[OH]. The red-brown solid on the anode dissolved in concentrated sulphuric acid to give a brown solution typical of manganese(III) in $\mathrm{H_2SO_4}$. No decrease in the concentration of the aqua-complex and no deposit at either electrode are observed if the electrolysis is carried out in 0.1N HCl.

These results seem to confirm the formation of anionic complexes such as those shown in equations (3)—(5). The anode reaction may be as (6) or (7) and the cathode

$$[\mathrm{Mn(CO)_3(OH)_3}]^{2-} \longrightarrow \mathrm{Mn^{III}[OH]_3} + 3\mathrm{CO} + 2e^- \qquad (6)$$

$$\begin{array}{l} [\mathrm{Mn(CO)_3(OH_2)(OH)_2}]^- \longrightarrow \\ \qquad \mathrm{Mn^{II}[OH]_2} + 3\mathrm{CO} + \mathrm{H_2O} + e^- \\ \qquad \downarrow \\ \qquad \mathrm{Mn^{III}[OH]_3} \end{array} \qquad (7)$$

$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H_2} \qquad (8)$$

reactions as in (8). The corresponding overall reaction is then (9). In the later stages of electrolysis, evolution of chlorine at the anode was detected. This suggests that, as electrolysis proceeds, the increasing acidity displaces the equilibria so far to the left that the concentration of anions containing manganese becomes so low that chlorine ions are preferentially discharged.

$$[\mathrm{Mn(CO)_3(OH_2)_3}]\mathrm{Cl} \longrightarrow \mathrm{Mn[OH]_3} + 3\mathrm{CO} + \mathrm{H_2} + \mathrm{HCl} \qquad (9)$$

The appearance of manganese compounds at the anode during electrolysis suggested that the aqua-complex might be in equilibrium with the $[\mathrm{Mn(CO)_5}]^-$ anion. We found that the u.v.–visible absorption spectrum of this anion in water is different from that of Figure 1(*b*), having $\lambda_{\mathrm{max.}} = 365$ nm. On acidifying the solution, the spectrum moves to longer wavelengths and broadens considerably, suggesting a mixture of products. A notable difference between these solutions and our aqua-complex is the great instability of the former towards atmospheric oxidation.

Photolysis.—When an aqueous solution of the aqua-complex (10^{-3} mol $\mathrm{dm^{-3}}$) is irradiated *in vacuo* at 25 °C with light of wavelength 435.8 nm a rapid first-order decomposition of the complex takes place. This is accompanied by the evolution of 1.3 mol of CO per mol of complex and by a marked increase in both the pH and conductivity of the solution, which becomes slightly turbid. If irradiation is continued until the solution shows no absorption in the u.v.–visible region and the solution is then extracted with benzene, the extract exhibits an absorption characteristic of $[\mathrm{Mn_2(CO)_{10}}]$, in a yield accounting for *ca.* 10% of the manganese present. Conductimetric titration of the aqueous phase with 0.01N $\mathrm{HNO_3}$ shows that 0.88 equivalents of base have been produced for each mol of (1) consumed. With silver(I) nitrate solution, this phase gives an immediate white precipitate as well as a black deposit of metallic silver. Evaporation to dryness *in vacuo* leads to a white residue which shows an organic carbonyl absorption at 1 600 $\mathrm{cm^{-1}}$. The solid reduced Fehlings solution and Tollens reagent and gives a positive response to spot tests for glyoxal.[9]

We propose that the reactions occurring during photolysis of the aqua-complex may be explained in terms of structure (1) as follows. Excitation may be followed by rapid protonation of the carbonyl [equation (10)] to give (2) which subsequently generates glyoxal,

$$(1) + h\nu \longrightarrow (1)^* \xrightarrow{\mathrm{H}^+} \underset{(2)}{[\mathrm{Mn(CO)_2(OH_2)_3(CHO)}]^{2+}\mathrm{Cl}^-} \qquad (10)$$

$$(2) \longrightarrow \mathrm{Mn^{II}} + \mathrm{H\dot{C}O} \qquad (11)$$

(10) and (11) is (12), consistent with the development of

$$2(1) \longrightarrow 2\mathrm{Mn^{II}} + 2[\mathrm{OH}]^- + 2\mathrm{Cl} + (\mathrm{HCO})_2 + 4\mathrm{H_2O} + 4\mathrm{CO} \qquad (12)$$

e.g. by liberating formyl radicals. When the proton concentration is reduced ($\mathrm{NH_3}$, 0.1 mol $\mathrm{dm^{-3}}$) no glyoxal is formed on irradiation. The overall reaction based on

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[9] F. Fiegl, 'Spot Tests in Organic Analysis,' 7th edn., Elsevier, Amsterdam, 1966.

basicity, the formation of glyoxal, and the evolution of CO during irradiation. However, the observed yields of base and CO are less than predicted by (12) which in any case cannot represent the total process since it does not allow for the formation of $[\mathrm{Mn_2(CO)_{10}}]$. A minor photoprocess might be the disproportionation (13).

$$4[\mathrm{Mn(CO)_3(OH_2)_3}]^+ \xrightarrow[\mathrm{H_2O}]{h\nu} 2[\mathrm{Mn(OH_2)_6}]^{2+} + [\mathrm{Mn_2(CO)_{10}}] + 2\mathrm{CO} \quad (13)$$

Reactions of $[\mathrm{Mn(CO)_5Cl}]$ *in Benzene Solution.*—When low concentrations of water (10^{-2} mol dm^{-3}) are added to a solution of $[\mathrm{Mn(CO)_5Cl}]$ in benzene an immediate change in the u.v.–visible spectrum occurs [Figure 5(*a*) and (*b*)]. Flushing the solution with dry nitrogen produces a shift in $\lambda_{\mathrm{max.}}$ to a longer wavelength (412 nm) to give spectrum 5(*c*) which is characteristic of the halide-bridged dimeric manganese(I) carbonyl halide complexes reported previously.[1] When the solution is almost saturated with water the spectrum changes to that in Figure 5(*d*) ($\lambda_{\mathrm{max.}}$ 401 nm) which is reminiscent of those of disubstituted manganese pentacarbonyl chlorides of type $[\mathrm{Mn(CO)_3ClL_2}]$ [L = a donor ligand (*e.g.* $\mathrm{Et_2O}$) [10]]. It has the same form as that of a benzene solution of the residue obtained by evaporating an aqueous solution of the aqua-complex to dryness *in vacuo*. Spectral observations suggest that this residue contains non-ionic $[\mathrm{Mn(CO)_3(HO_2)Cl}]$, formed in 25% yield.

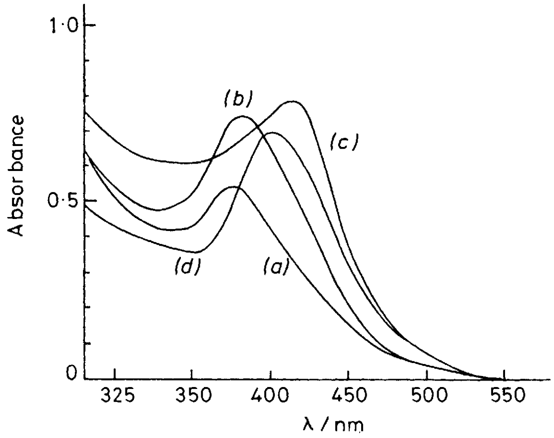
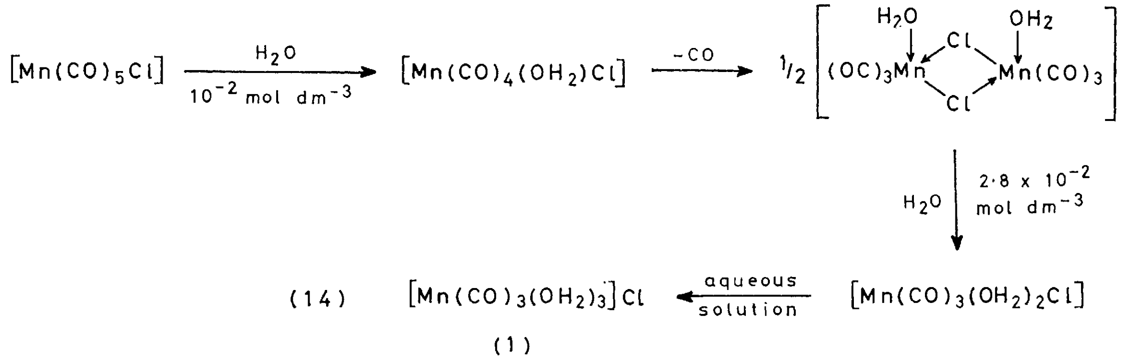


FIGURE 5 Spectral changes accompanying addition of water to a solution of $[\mathrm{Mn(CO)_5Cl}]$ in dry benzene: (*a*) $[\mathrm{Mn(CO)_5Cl}]$ (8.6×10^{-4} mol dm^{-3}) in dry benzene; (*b*) after addition of water (1.1×10^{-2} mol dm^{-3}); (*c*) after flushing (*b*) for 30 min with dry benzene-saturated $\mathrm{N_2}$; and (*d*) after addition of water (2.8×10^{-2} mol dm^{-3}) to (*c*)

The observations reported may therefore be rationalised as in equation (14), according to which the reactions of water in hydrocarbon solvents are completely analogous to those of other electron donors.[1,10]



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[10] M. Coldbeck, Ph.D. Thesis, Liverpool University, 1975.

[6/1566 *Received*, 10*th August*, 1976]