Journal of Organometallic Chemistry, 169 (1979) 185—190

OXIDATION OF MANGANESE METAL BY DIMERIC METAL CARBONYLS IN THF; ESR SPECTRA OF THE RESULTING MANGANESE(II) SPECIES

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(Received October 10th, 1978)

Summary

Reaction of $Mn_2(CO)_{10}$ with Mn in THF gives rise to the same species as photolysis of $Mn_2(CO)_{10}$ in the same solvent. Similarly Mn with $Co_2(CO)_8$ or $[Mo(CO)_3Cp]_2$ gives solutions containing Mn^{2+} and $Co(CO)_4^-$ or $Mo(CO)_3Cp^-$. The temperature dependence of the intensity of the ESR spectrum of the solutions with $Mn(CO)_5^-$ or $Co(CO)_4^-$ is explained in terms of an equilibrium involving 6- and 5-coordinate solvated Mn^{2+} ions.

Introduction

The controversy over the identity of the paramagnetic species arising from photolysis of $Mn_2(CO)_{10}$ in THF [1] has now been resolved in favour of a Mn^{2+} species with $Mn(CO)_5^-$ as the counter-ion [2—5] formed by a disproportionation reaction (eq. 1).

$$3\,Mn_2(CO)_{10} \xrightarrow[THF]{h\nu} 2\,Mn^{2+} + 4\,Mn(CO)_5^- + 10\,CO \qquad (1)$$

However, some aspects of the system are as yet unexplained. Firstly, the ESR line widths of the Mn^{2+} hyperfine components are exceptionally narrow (~3 G for the $M_I = 1/2$ line compared with the more usual value of ⩾10 G for Mn^{2+} in organic solvents) enabling resolution of fine structure arising from the non-degeneracy of the five allowed electron spin transitions [2,4]. Secondly, the ESR signal strength diminishes rapidly on warming of the sample above 25°C but reappears reversibly on cooling. This paper reports non-photolytic preparations of solutions of Mn^{2+} in THF with $Mn(CO)_5^-$, $Co(CO)_4^-$ or $Mo(CO)_3Cp^-$ as counter-ions, together with the results of a detailed analysis of the variable-temperature behaviour which gives a good indication of the processes involved.

Results and discussion

Oxidation of manganese metal with $Mn_2(CO)_{10}$, $Co_2(CO)_8$ and $[Mo(CO)_3Cp]_2$

The reduction of metal carbonyl dimers by electropositive metals is well-known [6]. Usually sodium (as an amalgam) or other Group I metals are used although other metals including Mg [7—9], Mn [7,10] and even lanthanides [10] have been employed. It seemed reasonable, therefore, to prepare solutions containing Mn^{2+} and $Mn(CO)_5^-$ in THF by reaction of manganese metal with $Mn_2(CO)_{10}$ (eq. 2).

$$Mn + Mn_2(CO)_{10} \xrightarrow{THF} Mn^{2+} + 2\ Mn(CO)_5^- \qquad (2)$$

It was found that such a reaction did occur (in the dark) and that the ESR spectrum of the resulting solution was exactly superimposable on that of solutions prepared by photolysis of $Mn_2(CO)_{10}$ (eq. 1) *. This independent synthesis confirms beyond doubt the earlier assignment [2,4,5] and eliminates the complexities arising from solvent photolysis [5]. Furthermore, reaction of $Co_2(CO)_8$ or $[Mo(CO)_3Cp]_2$ (or $Hg(Mo(CO)_3Cp)_2$) with manganese metal in THF also occurred over 24 hours at room temperature, with a resulting discharge of the intense colour of the dimeric species as the colourless anions ($Co(CO)_4^-$ and $Mo(CO)_3Cp^-$ respectively) formed ** (c.f. ref. 7—10). Significantly the ESR spectrum arising from Mn^{2+} with $Co(CO)_4^-$ as counter-ion was identical in all respects to that of Mn^{2+} with $Mn(CO)_5^-$. In contrast the line-widths of the Mn^{2+} signal with $Mo(CO)_3Cp^-$ in THF were considerably broader and the spectrum resembled those of Mn^{2+} with inorganic counter-ions (SCN^-, Cl^-, etc.) [11—16].

Similar experiments with $Re_2(CO)_{10}$ or $[Fe(CO)_2Cp]_2$ and Mn metal in THF gave no reaction, which is consistent with the results obtained by Dessy et al. [17] who showed electrochemically that the ease of reduction of dimeric metal carbonyls decreases in the order $Co_2(CO)_8 > [Mo(CO)_3Cp]_2 > Mn_2(CO)_{10} > [Fe(CO)_2Cp]_2 > Re_2(CO)_{10}$. It appears that dimers with $-E_{1/2} < 1.7$ on Dessy's scale will oxidise Mn to Mn^{2+}.

Temperature dependence of the Mn^{2+} ESR signal

It has been noted by several groups [2—5] that the intensity of the ESR spectrum from Mn^{2+} with $Mn(CO)_5^-$ in THF diminishes reversibly with increasing temperature over the range 10°C—60°C. This is unlikely to arise from a chemical change in the Mn^{2+} ion involving change in oxidation state, and is most reasonably explained in terms of a change in coordination geometry introducing fast relaxation processes with a concomitant broadening of the lines to an extent that the signal becomes undetectable.

It was assumed that the equilibrium process involved was dissociation of a

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* Similar results have been obtained using a metal vapour synthesis approach. Thus co-condensation of Mn vapour, $Mn_2(CO)_{10}$ and THF gives an identical spectrum [20].

** $Co_2(CO)_8$ undergoes disproportionation to Co^{2+} and $Co(CO)_4^-$ in THF but it appears reduction with Mn is more rapid. No evidence of CO evolution was found and no signal arising from Co^{2+} was observed by ESR.

ligand from $Mn(THF)_6^{2+}$ to give a five-coordinate ion (eq. 3).

$$Mn(THF)_6^{2+} \rightleftharpoons Mn(THF)_5^{2+} + THF \qquad (3)$$

The ESR signal originates from the 6-coordinate species whereas the 5-coordinate moiety is not detected (cf. ref. 12,13). The equilibrium constant for the dissociation (eq. 3) was determined by measuring the intensity of the signal at various temperatures relative to that at 263 K where Mn^{2+} appears to be completely present as the 6-coordinate species. The results obtained are presented in Table 1. A plot of ln K versus $1/T$ gave a straight line (Fig. 1) from which the thermodynamic parameters $\Delta H = 106 \pm 4$ kJ mol^{-1} and $\Delta S = 386 \pm 14$ J K^{-1} mol^{-1} are readily obtained. These values lend credence to the assumption that the process involved is that defined by eq. 3. Although data for THF solvates is sparse, it has been calculated [18] that for the dissociation outlined in eq. 4, the ΔH change is ca. 150 kJ mol^{-1} which suggests that $\Delta H = 106$ kJ mol^{-1} is a reasonable enthalpy change for the removal of one THF ligand from

$$Fe(H_2O)_6^{2+}(aq) \longrightarrow Fe(H_2O)_5^{2+}(aq) + H_2O(aq) \qquad (4)$$

$Mn(THF)_6^{2+}$. Similarly, the large positive entropy change is also consistent with a dissociation process. No equilibrium process involving formation or dissociation of ion-pairs is expected to be governed by ΔH and ΔS changes similar to those observed. Furthermore, the fact that solutions with $Mn(CO)_5^-$ or $Co(CO)_4^-$ have identical ESR characteristics also suggests that ion-pairing has no influence on the solvated Mn^{2+} ion in systems containing these anions. Hence the ESR spectrum can be confidently assigned to an unperturbed $Mn(THF)_6^{2+}$ species in these systems. It is worth noting that the process described by eq. 4 is the first step in an S_N1 mechanism for ligand substitution or solvent exchange at an octahedral complex, a subject which has been intensively studied (e.g. ref. 18).

TABLE 1

THERMODYNAMIC DATA FOR $Mn(THF)_6^{2+} \rightleftharpoons Mn(THF)_5^{2+}$ + THF

T (K)	$Mn(THF)_6^{2+}$ [a]	$Mn(THF)_5^{2+}$ [b]	K [c]	ΔG (kJ mol^{-1}) [d]
263	1000	0	—	—
268	983	17	0.21	3.4
273	928	72	0.96	0.1
278	814	186	2.82	−2.4
283	649	351	6.67	−4.5
288	460	540	14.5	−6.4
293	272	728	33.0	−8.5
298	158	842	65.7	−10.4
303	84	916	134	−12.4
308	48	952	245	−14.1
313	27	973	444	−15.9

$\Delta H_{diss} = 106 \pm 4$ kJ mol^{-1} $\qquad$ $\Delta S_{diss} = 386 \pm 14$ J K^{-1} mol^{-1}

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[a] Relative to 1000 at 263 K. [b] By difference. [c] $K = [Mn(THF)_5^{2+}][THF]/[Mn(THF)_6^{2+}]$ with [THF] = 12.3 mol l^{-1}. [d] From $\Delta G = -RT \ln K$.

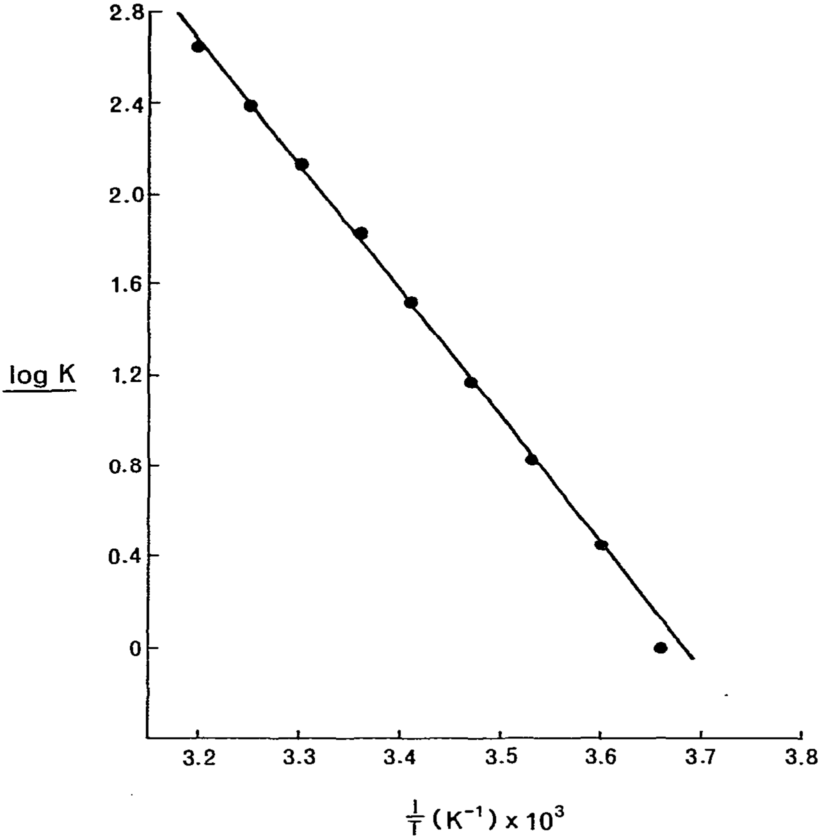

Fig. 1. Plot of log K vs. $1/T$ for $Mn(THF)_6^{2+} \rightleftharpoons Mn(THF)_5^{2+} + THF$.

An examination of molecular models of $Mn(THF)_6^{2+}$ shows that the coordination sphere will be sterically crowded, a conclusion in agreement with the facile thermal dissociation observed. The narrow linewidths and general features of the ESR spectrum of $Mn(THF)_6^{2+}$ with $Mn(CO)_5^-$ (recently summarised by Simpson et al. [5]) can be explained on this basis. Firstly, the signal is unique to THF because these solvent molecules neatly fill the coordination sphere of the cation so that dynamic fluctuations of the octahedral ligand field are minimised *. Solvent exchange by associative mechanisms will also be unfavourable; with less bulky solvents perturbations arising from these processes are a major contributor to the line-width [13]. Secondly, on addition of small amounts of other solvents (2-Me-THF, H_2O, etc.) to solutions of $Mn(THF)_6^{2+}$, mixed species of the type $Mn(THF)_n(Solv)_{6-n}^{2+}$ will form, disturbing the octahedral ligand-field symmetry. This process will also lead to significant line broadening. Similarly the presence of counter-ions more basic and less bulky than $Mn(CO)_5^-$ or $Co(CO)_4^-$ will lead to the formation of lower symmetry

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* Photolysis of $Mn_2(CO)_{10}$ in less bulky (trimethylene oxide [4]) or more bulky (2-Me-THF [5]) solvents than THF gives broader lines.

ion-paired species. This explains the broadening of lines arising from addition of ClO_4^- [3—5] (which is known to associate with Mn^{2+} in organic solvents [11]), and also explains the loss of signal observed on exposure of a solution of Mn^{2+} with $Mn(CO)_5^-$ to air. In this latter case oxidation of the air-sensitive anion will introduce O^{2-} or OH^- leading to species of the type $[Mn(THF)_5OH]^+$ or $[Mn(THF)_5O]$ which are expected to give indetectably broad ESR signals [11]. In this context it is worth noting that the presence of $Mo(CO)_3Cp^-$ leads to relatively broad lines. This anion is apparently a stronger base (through a carbonyl oxygen atom, c.f. ref. 8) than $Mn(CO)_5^-$ or $Co(CO)_4^-$, an observation that can be rationalised in terms of the average carbonyl stretching frequencies of the respective anions [19].

It can thus be concluded that the unusual ESR behaviour first noted in photolysed solutions of $Mn_2(CO)_{10}$ in THF is the result of two fortuitous factors. Firstly, THF molecules are of just the right size to completely fill a regular octahedral coordination sphere of a Mn^{2+} ion at room temperature, and secondly the large counter-ion $Mn(CO)_5^-$ shows no tendency to associate with the Mn^{2+} solvate.

Further studies are underway to examine the oxidation of other metals with dimeric metal carbonyls and to isolate crystalline products from the systems discussed in this paper for full characterisation.

Experimental

$Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were obtained commercially (Pressure Chemical Co.) and were sublimed in vacuo prior to use. $[Mo(CO)_3Cp]_2$ was recrystallised from $CHCl_3$ and dried by pumping in vacuo for several hours. Manganese metal (—50—+325 mesh) was obtained from Alfa Division. THF was purified by distillation from sodium benzophenone ketyl. ESR spectra were recorded on a Varian Associates E104 spectrometer equipped with an E257 variable-temperature accessory.

Preparation of ESR samples

Utmost precautions were taken to exclude traces of H_2O and O_2 from samples as these inhibited the reaction between manganese metal and the carbonyl dimers. In a typical preparation Mn metal (0.01 g) and $Mn_2(CO)_{10}$ (0.002 g, 0.005 mmol) were placed in an oven-dried 4 mm o.d. pyrex tube fitted with a ground-glass joint. After pumping under high vacuum for at least 30 min, THF (ca. 0.5 cm^3) was distilled into the tube directly from purple benzophenone ketyl. After two freeze-pump-thaw cycles the evacuated tube was sealed. Reaction in each case appeared essentially complete after 24 h in the dark at 20°C although no detailed studies were undertaken.

Variable temperature study

The fourth line from low field was recorded at 5°C intervals. Care was taken to ensure all machine variables (modulation, detector current, microwave power, etc.) were constant for all measurements. The peak-to-peak amplitude was taken to be proportional to the concentration of $Mn(THF)_6^{2+}$ since it was found that the line-width at half-height did not vary significantly over the temperature range employed.

Acknowledgements

This work was financially supported by the New Zealand Universities' Grants Committee. I also wish to thank Dr. G. Bowmaker of the University of Auckland for use of ESR facilities, Professor M.F. Lappert and Dr. A. Hudson who first stimulated my interest in this area, and Dr. J. Simpson and co-workers for exchange of information.

References

1 S.A. Hallock and A. Wojcicki, J. Organometal. Chem., 54 (1973) C27.
2 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Organometal. Chem., 92 (1975) C11.
3 C.L. Kwan and J.K. Kochi, J. Organometal. Chem., 101 (1975) C9.
4 A. Hudson, M.F. Lappert, J.J. MacQuitty, B.K. Nicholson, H. Zainal, G.R. Luckhurst, C. Zannoni, S.W. Bratt and M.C.R. Symons, J. Organometal. Chem., 110 (1976) C5.
5 A.S. Huffadine, B.M. Peake, B.H. Robinson, J. Simpson and P.A. Dawson, J. Organometal. Chem., 121 (1976) 391.
6 See J. Ellis, J. Organometal. Chem., 86 (1975) 1 for a recent review.
7 T. Blackmore and J.M. Burlitch, J. Chem. Soc. Chem. Commun., (1973) 405.
8 S.W. Ulmer, P.M. Skarstad, J.M. Burlitch and R.E. Hughes, J. Amer. Chem. Soc., 95 (1973) 4469.
9 G.B. McVicker, Inorg. Chem., 14 (1975) 2087.
10 A.E. Crease and P. Legzdins, J. Chem. Soc. Chem. Commun., (1973) 775.
11 H. Levanon and Z. Luz, J. Chem. Phys., 49 (1968) 2031.
12 L. Burlamacchi, J. Chem. Phys., 55 (1971) 1205.
13 S.I. Chan, B.M. Fung and H. Lutje, J. Chem. Phys., 47 (1967) 2121.
14 B.B. Garrett and L.O. Morgan, J. Chem. Phys., 44 (1966) 890.
15 R.G. Hughes and R.J. Myers, J. Chem. Phys., 40 (1964) 877.
16 L. Lynds, J.E. Crawford, R.M. Lynden-Bell and S.I. Chan, J. Chem. Phys., 57 (1972) 5216.
17 R.E. Dessy, P.M. Weissmanand and R.L. Pohl, J. Amer. Chem. Soc., 88 (1966) 5117.
18 F. Basolo and R.G. Pearson, "Mechanisms of Inorganic Reactions", J. Wiley and Sons, New York, 1967, p. 132.
19 D.F. Shriver and A. Alich, Inorg. Chem., 11 (1972) 2984; D.F. Shriver, J. Organometal. Chem., 94 (1975) 259.
20 J.J. MacQuitty, personal communications, 1977.