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Kinetics of Reactions of Manganese Pentacarbonyl Halides with Cyanide.

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SUMMARY

The kinetics of the reactions of the manganese pentacarbonyl halides $Mn(CO)_5X$, X = Cl, Br, or I, with cyanide to give the $[Mn(CO)_4(CN)_2]^-$ anion are reported. The respective rate laws and rate constants indicate that the intermediate in the reaction of $Mn(CO)_5Cl$ is $Mn(CO)_5(CN)$, but that the intermediates in the reactions of $Mn(CO)_5Br$ and $Mn(CO)_5I$ are the $[Mn(CO)_4(CN)Br]^-$ and $[Mn(CO)_4(CN)I]^-$ anions respectively.

INTRODUCTION

The cyanide ion is a good nucleophile for attack at transition metal complexes; we have previously reported on the kinetics of its reactions with such complexes as the $Fe(bipy)_3^{2+}$ cation[1] and $Mo(CO)_4(5NO_2phen)$.[2] We have also described the kinetics of the two stages of the reaction of the rhenium(I) pentacarbonyl halides $Re(CO)_5X$ with cyanide to give the $Re(CO)_4(CN)_2^-$ anion.[3] We now report on the reaction sequences and kinetics for the analogous manganese(I) compounds, $Mn(CO)_5X$ with X = Cl, Br, or I, with cyanide in various solvent media.

RESULTS AND DISCUSSION

Mechanisms. The carbonyl halides $Mn(CO)_5X$, X = Cl, Br, or I, react with cyanide to give the $Mn(CO)_4(CN)_2^-$ anion.[4] Presumably these reactions, like those of the analogous rhenium compounds,[3] take place in two stages.

There are two plausible two-step routes, one through $Mn(CO)_5(CN)$, the other through an $Mn(CO)_4(CN)X^-$ anion. For the rhenium carbonyl halides there is a considerable body of evidence for the intermediacy of $Re(CO)_4(CN)X^-$, none for the intermediacy of $Re(CO)_5(CN)$.[3,5] For the reactions of the manganese carbonyl halides, the first need is to establish the reaction sequence for each compound, which can be achieved by comparing rate laws and rate constants for the three compounds. However there is one significant observation that should precede the description of kinetic patterns, and that is that carbon monoxide is evolved immediately on adding cyanide to solutions of $Mn(CO)_5Br$ or of $Mn(CO)_5I$, but not on adding cyanide to a solution of $Mn(CO)_5Cl$.

The reaction of $Mn(CO)_5Cl$ with cyanide (large excess) in methanol proceeds in one step, following first-order kinetics. The variation of the observed rate constant with cyanide concentration is reported in Table 1. The Figure shows that the major path is second-order in cyanide; the rate law is:

$$-d[Mn(CO)_5Cl]/dt \quad = \quad \{\underline{k}_1 + \underline{k}_3[CN^-]^2\}[Mn(CO)_5Cl]$$

This pattern is different from that reported[3] for the reaction of $Re(CO)_5Cl$ with cyanide; an appropriate mechanism is outlined below.

Table 1 The dependence of observed first-order rate constants for the reaction of $Mn(CO)_5Cl$ with cyanide on cyanide concentration in methanol at 298.5 K, $\underline{I}$ = 0.032 mol dm^{-3} (Bu^n_4NBr).

$[Et_4NCN]$/mol dm^{-3}	0.003	0.008	0.016	0.019	0.022	0.026	0.032
$10^3\underline{k}_{obs}/s^{-1}$	0.59	0.69	1.04	1.51	1.84	2.51	3.34

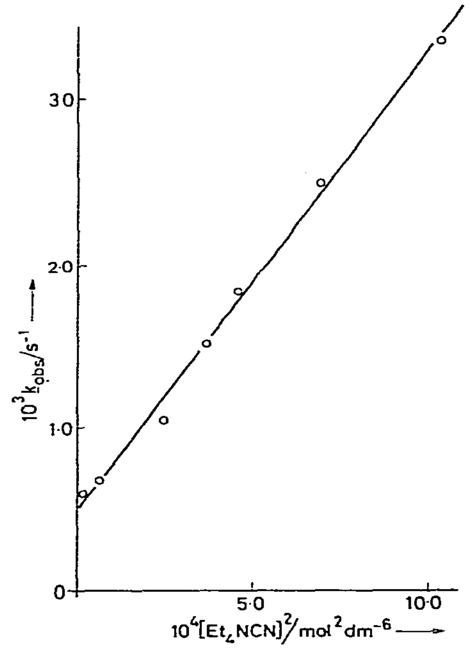

Figure 1 The dependence of observed first-order rate constants, $\underline{k}_{obs}$, on the square of the cyanide concentration in the reaction of $Mn(CO)_5Cl$ with cyanide.

The reaction of $Mn(CO)_5Br$ with cyanide (large excess) in methanol follows first-order kinetics after the first few seconds. Observed first-order rate constants for the main portion of each run are listed in Table 2; we are unable to get sufficiently good data for the first step for a satisfactory analysis of the consecutive first-order processes to be possible.

Table 2 The dependence of observed first-order rate constants for the second stage of the reaction of $Mn(CO)_5Br$ with cyanide on cyanide concentration in methanol at 298.5 K, $\underline{I}$ = 0.032 mol dm^{-3} (Bu^n_4NBr).

$[Et_4NCN]/mol\ dm^{-3}$	0.008	0.016	0.027	0.032
$10^3\underline{k}_{obs}/s^{-1}$	1.3	2.0	2.9	3.4

For the main (second) portions of these runs the major reaction path is first-order in cyanide, the full rate law being

$$\text{rate} = \{\underline{k}_1 + \underline{k}_2[\text{CN}^-]\}[\text{Mn compound}]$$

The reaction of $Mn(CO)_5I$ with cyanide (large excess) in methanol has a kinetic pattern corresponding to consecutive first-order reactions. The kinetics were analysed by standard procedures[3,6] to obtain the first-order rate constants for each step. At 298.5 K, in methanol solution, the rate constants were 5.4×10^{-3} and 5.0×10^{-4} s^{-1} in 0.016 mol dm^{-3} KCN, 8.1×10^{-3} and 6.5×10^{-4} s^{-1} in 0.022 mol dm^{-3} KCN (in both cases at an ionic strength of 0.032 mol dm^{-3}, maintained with tetra-n-butylammonium bromide). Thus in both steps a major route depends on cyanide concentration. The pattern here is very similar to that established for the reactions of rhenium pentacarbonyl halides with cyanide (See Fig. 2).

The kinetics described in the preceding paragraph indicate similar mechanisms for the reaction of $Mn(CO)_5Br$ and $Mn(CO)_5I$ with cyanide, but a different mechanism for the reaction of $Mn(CO)_5Cl$ with cyanide. The mechanism for the first two must be the same as that established for the

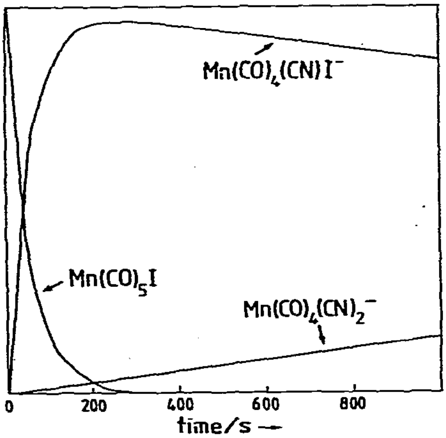

Figure 2 The time dependence of starting compound, intermediate, and product, for the two-stage reaction of $Mn(CO)_5I$ with cyanide.

rhenium compounds, with parallel solvolysis* and direct cyanide attack paths and the intermediates $Mn(CO)_4(CN)Br^-$ and $Mn(CO)_4(CN)I^-$ respectively. The different rates of the second steps rule out the common intermediacy of $Mn(CO)_5(CN)$, but the results for $Mn(CO)_5Cl$ suggest a mechanism:

$$\begin{tikzcd}
Mn(CO)_5Cl + CN^- \arrow[r, shift left, "fast"] & Mn(CO)_5(CN) + Cl^- \arrow[l, shift left, "K"] \arrow[d, "slow\ (\underline{k})", "CN^-"'] \\
 & Mn(CO)_4(CN)_2^- + CO
\end{tikzcd}$$

This mechanism, with a parallel solvolysis path, conforms to the rate law given above, with K $\underline{k}$ equal to $\underline{k}_3$. The different route here suggests that the trans-labilising trend $I^- > Br^- > Cl^-$ leads to such low labilisation of CO trans- to Cl that in fact the CO labilises the Cl; $I^- > Br^- > CO > Cl^-$ here. Differences in mechanisms and in reaction conditions (solvents and temperatures) prevent direct manganese versus rhenium reactivity comparisons.

Reaction in alcohols. The kinetic pattern for the reaction of $Mn(CO)_5Br$ with cyanide in ethanol, n-propanol, and n-butanol is the same as that in methanol, with a quick first reaction followed by a second step whose major component is first-order in cyanide. Second-order rate constants for this path, the bimolecular reaction of $Mn(CO)_4(CN)Br^-$ with CN^-, increase steadily but not dramatically in the order MeOH < EtOH < n-PrOH < n-BuOH. The chemical potential of the cyanide ion presumably increases steadily in the same order and sense,[7] which could qualitatively account for the observed rate trend. The Gibbs free energy of transfer (ΔG_{tr}) of cyanide from methanol to ethanol is 2.8 or 2.9 kJ mol^{-1},[7] which, assuming $\Delta G_{tr} = 0$ for the $Mn(CO)_4(CN)Br^-$ anion and for the transition state, would lead to an increase in the second-order rate constant of four times. The results in

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* Uncertainties in estimated values for $\underline{k}_1$ in the reactions of $Mn(CO)_5Br$ and $Mn(CO)_5I$ are too large for a discussion of these to be worthwhile.

Table 3 Observed first-order rate constants and derived second-order rate constants for the second stage of the reaction of $Mn(CO)_5Br$ with cyanide in alcohols, $\underline{I}$ = 0.032 mol dm^{-3} (Bu^n_4NBr).

Solvent	T/K	[KCN]/mol dm^{-3} 0.001	0.003	0.006	0.008	0.011	0.016	0.022	0.027	0.032	$\underline{k}_2$
		$10^4\underline{k}_{obs}/s^{-1}$									$dm^3 mol^{-1} s^{-1}$
Methanol											
	311.2		37		47		72	84	104		0.29
	318.2			63		80		127		200	0.49
	334.2	27				144	210	290	320		1.20
Ethanol											
	298.5		20		33		53	66	75	88	0.21
n-Propanol											
	298.5	24	34			44	62	71	93		0.23
n-Butanol											
	298.5	20			44		69	90		124	0.34

Table 3 indicate that the actual increase in second-order rate constant is about three times. Thus the Gibbs free energy transfer of the cyanide could be the dominant factor determining relative reactivities here. Unfortunately it is impossible to determine Gibbs free energies of transfer for the $Mn(CO)_4(CN)Br^-$ intermediate, so it is not possible to pursue this initial state-transition state analysis further.

The dependence of $\underline{k}_2$ for the reaction of $Mn(CO)_4(CN)Br^-$ with CN^- on temperature (Tables 2 and 3) indicates an activation enthalpy of 58 ± 5 kJ mol^{-1} and an activation entropy of -70 ± 14 J K^{-1} mol^{-1} in methanol. These values seem reasonable in the light of the reported values of $\Delta H^{\ddagger}$ = 61 kJ

mol^{-1} and $\Delta S^{\ddagger} = -84$ J K^{-1} mol^{-1} for the reaction of $Re(CO)_4(CN)I^-$ with CN^- in 70% methanol.[3]

Reaction in (aqueous) dimethyl sulphoxide. Solvolysis of $Mn(CO)_5Br$ in dimethyl sulphoxide occurs at a negligible rate compared with cyanide attack. Hence the observed first-order rate constants for cyanide attack (second stage) can be converted directly to second-order rate constants for the reaction of $Mn(CO)_4(CN)Br^-$ with CN^- (Table 4). The value of $\underline{k}_2$ for reaction in dimethyl sulphoxide is much smaller than that for the reaction in methanol, 2.5×10^{-3} and 1.2 dm^3 $mol^{-1}s^{-1}$ respectively at 334.2K. This result is surprising in view of the higher chemical potential of the cyanide ion in dimethyl sulphoxide than in water.[7] Presumably this chemical potential difference is over-ridden by changes in chemical potentials of the $Mn(CO)_4(CN)Br^-$ anion and (or) the transition state. Speculation here is ruled out by the enormous difference between the two available estimates, +2.5 or +14 kJ mol^{-1}, for the Gibbs free energy of transfer of cyanide from methanol into dimethyl sulphoxide.[7]

Table 4 Observed first-order rate constants and derived second-order rate constants for the second stage of the reaction of $Mn(CO)_5Br$ with cyanide (0.032 mol dm^{-3} Et_4NCN) in dimethyl sulphoxide.

T/K	298.5	302.6	304.7	306.2	309.0	318.2	334.2
$10^5\underline{k}_{obs}/s^{-1}$	3.0	4.1	5.8	7.5	13	54	250
$10^3\underline{k}_2/mol\ dm^{-3}s^{-1}$	0.9	1.3	1.8	2.3	4.1	16.9	78

Addition of water to solvent dimethyl sulphoxide results in an increase in the second-order rate constant for the reaction of $Mn(CO)_4(CN)Br^-$ with CN^- (Table 5). Increasing reactivity with increasing solvent polarity here is a

Table 5 Observed first-order rate constants and derived second-order rate constants for the second stage of the reaction of $Mn(CO)_5Br$ with cyanide (0.032 mol dm^{-3} Et_4NCN) in dimethyl sulphoxide + water mixtures at 334.2 K.

% water (v/v)	0	10	20	30
$10^5 \underline{k}_{obs}/s^{-1}$	250	320	440	570
$10^3 \underline{k}_2/mol\ dm^{-3}s^{-1}$	78	100	138	178

trend consistent with the above comparison of dimethyl sulphoxide with methanol. However this qualitative correlation of rate constant with solvent polarity cannot be turned into a satisfactory quantitative correlation with such established empirical solvent parameters as the kinetically based Y values of Grunwald and Winstein.[8] Unfortunately attempts at correlation with spectroscopically based solvent $\underline{E}_T$ values[9] or thermochemically based Gutmann donor numbers DN[10] are precluded by the lack of values for dimethyl sulphoxide - water mixtures.

The temperature dependence of rate constants (Table 4) indicates activation parameters $\Delta H^{\ddagger} = 106 \pm 5$ kJ mol^{-1} and $\Delta S^{\ddagger} = +52 \pm 14$J K^{-1} mol^{-1} for the reaction of $Mn(CO)_4(CN)Br^-$ with CN^- in dimethyl sulphoxide solution. These values are remarkably different from those in methanol (v.s.), showing that enthalpies and entropies of solvation of the reactants and/or transition state are important in determining reactivities here. In the absence of enthalpy of solution and transfer data for CN^- and for $Mn(CO)_4(CN)Br^-$, an absence which could fairly readily be remedied for the former but not for the latter, it is not possible to discuss this difference in activation parameters satisfactorily.

EXPERIMENTAL

Manganese pentacarbonyl chloride was prepared from dimanganese decacarbonyl and chlorine;[11] manganese pentacarbonyl bromide was purchased from Strem Chemicals Inc.; manganese pentacarbonyl iodide was prepared from dimanganese decacarbonyl and iodine.[11] Tetraethylammonium cyanide was obtained from Fluka, tetrabutylammonium bromide from Eastman Kodak. Solvents were purified by standard procedures.[12]

Kinetic runs were conducted in 10 mm cells in the thermostatted cell compartment of a Unicam SP800A or SP8-100 spectrophotometer. First-order rate constants for one-step processes were computed (Cyber 72) using a standard least-mean-squares program; rate constants for the consecutive first-order processes were computed as described previously.[3,6]

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