Kinetics of Reaction of Rhenium Pentacarbonyl Halides with Cyanide Ion in Aqueous Methanol †

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The reactions of rhenium pentacarbonyl halides with a large excess of cyanide ion in aqueous methanolic solution follow a kinetic pattern characteristic of consecutive first-order processes [equation (i)]. Rate laws and kinetic

$$[\mathrm{Re(CO)_5X}] \xrightarrow{\mathrm{CN^-}} [\mathrm{Re(CN)(CO)_4X}]^- \xrightarrow{\mathrm{CN^-}} [\mathrm{Re(CN)_2(CO)_4}]^- \quad \text{(i)}$$

parameters are reported for these reactions, with X = Cl, Br, or I.

It has long been known that the final product of the reaction of rhenium pentacarbonyl chloride with an excess of cyanide ion is the $[\mathrm{Re(CN)_2(CO)_4}]^-$ anion.[1] More recently the generation of the $[\mathrm{Re(CN)(CO)_4I}]^-$ anion by the reaction of rhenium pentacarbonyl iodide with sodium cyanide has been reported.[2] The corresponding anions $[\mathrm{Re(CN)(CO)_4Cl}]^-$ and $[\mathrm{ReBr(CN)(CO)_4}]^-$ have also been characterised.[2] We have examined the kinetics of reactions of rhenium pentacarbonyl chloride, bromide, and iodide with an excess of cyanide ion in aqueous methanolic solution. We find that each of these systems exhibits a kinetic pattern corresponding to consecutive first-order reactions. Both chemical evidence [1,2] and our kinetic results indicate that the $[\mathrm{Re(CN)(CO)_4X}]^-$ anion rather than $[\mathrm{Re(CN)(CO)_5}]$ is the intermediate. Thus the reaction sequence we are monitoring is that shown in equation (1). We have

$$[\mathrm{Re(CO)_5X}] \xrightarrow{\mathrm{CN^-}} [\mathrm{Re(CN)(CO)_4X}]^- \xrightarrow{\mathrm{CN^-}} [\mathrm{Re(CN)_2(CO)_4}]^- \quad (1)$$

analysed our kinetic results according to the method recently developed by Alcock *et al.*[3] In the present paper we report rate laws, rate constants, and activation parameters for these reactions of rhenium pentacarbonyl halides with cyanide ion.

EXPERIMENTAL

Reagents.—The rhenium pentacarbonyl halides were prepared by heating the appropriate potassium hexahalogenorhenate(IV) with copper powder and carbon monoxide under pressure.[4] Potassium cyanide and potassium nitrate were AnalaR materials, used as supplied. Methanol was dried over magnesium and iodine previous to redistillation.

Kinetics.—These were monitored spectrophotometrically, with reaction mixtures contained in 1-cm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. The kinetic pattern observed corresponded to two consecutive reactions, with the second being of the order of a hundred times slower than the first. The majority of the kinetic results was obtained from optical densities monitored at 350 nm, at which wavelength the increase and subsequent decrease in optical density with time were well marked. In order to gain some information solely on the first step of the reaction of $[\mathrm{Re(CO)_5I}]$ with cyanide ion, some runs were conducted at 301 nm, the isosbestic point of the second stage of this reaction in 70% methanol–water. Final spectra of reaction mixtures from $[\mathrm{Re(CO)_5Cl}]$, $[\mathrm{ReBr(CO)_5}]$, and $[\mathrm{Re(CO)_5I}]$ were identical, as expected for generation of the common product, $[\mathrm{Re(CN)_2(CO)_4}]^-$.

All runs were conducted with the cyanide present in large excess over the rhenium pentacarbonyl halide. Under these conditions the variation of optical density with time could in all cases be satisfactorily analysed in terms of two consecutive first-order processes. We derived values for the respective first-order rate constants using a recently published method,[3] appropriately modified to suit the present situation.

Solubilities.—These were estimated spectrophotometrically for $[\mathrm{Re(CO)_5I}]$ and $[\mathrm{ReBr(CO)_5}]$ for thermostatted saturated equilibrated solutions. In 70% methanol, $[\mathrm{Re(CO)_5I}]$ had $\lambda_{\max.} = 330$ nm (ε 2 000 dm^3 mol^{-1} cm^{-1}) and $[\mathrm{ReBr(CO)_5}]$ had $\lambda_{\max.} = 320$ nm (ε 1 600 dm^3 mol^{-1} cm^{-1}). In 50% methanol, $[\mathrm{Re(CO)_5I}]$ had $\lambda_{\max.} = 328$ nm (ε 2 000 dm^3 mol^{-1} cm^{-1}).

RESULTS

Computed first-order rate constants ($k_{\mathrm{obs.}}$) for the reactions of rhenium pentacarbonyl halides with cyanide ion are reported in Table 1. For the first stage of the reaction [*cf.* equation (1)], plots of $k_{\mathrm{obs.}}$ against cyanide concentration were linear, with the best straight line passing, within experimental uncertainty, through the origin.‡ The intercept of the least-mean-squares computed straight line on the $k_{\mathrm{obs.}}$ axis is within its 90% confidence limits of zero in each case, indicating the rate law for this reaction to be as shown in equation (2). For the second stage of the reaction, plots of $k_{\mathrm{obs.}}$ against cyanide concentration were again linear, but this time with a significant intercept, indicating the operation of a rate law of the type (3). Indeed for the bromide and chloride, the k_{21} term is much more important than the $k_{22}[\mathrm{CN^-}]$ term in the rate law.

$$-\mathrm{d}[\mathrm{Re(CO)_5X}]/\mathrm{d}t = k_{12}[\mathrm{Re(CO)_5X}][\mathrm{CN^-}] \quad (2)$$

$$-\mathrm{d}[\mathrm{Re(CN)(CO)_4X^-}]/\mathrm{d}t = (k_{21} + k_{22}[\mathrm{CN^-}])[\mathrm{Re(CN)(CO)_4X^-}] \quad (3)$$

Activation parameters were computed from the temperature variation of the various rate constants for the

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† No reprints available.

‡ We have estimated a rate constant of *ca.* 2×10^{-5} s^{-1} for the presumably dissociative reaction of $[\mathrm{Re(CO)_5I}]$ with triphenylphosphine in 70% methanol at 323 K. Such a small rate constant for dissociative loss of carbon monoxide explains the absence of a detectable $k_{11}[\mathrm{Re(CO)_5I}]$ term in the rate law (2). This rate constant of 2×10^{-5} s^{-1} for replacement of CO by $\mathrm{PPh_3}$ in aqueous methanol compares reasonably with known rate constants for carbon monoxide exchange in different solvents.[5]

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Table 1

Observed first-order rate constants ($k_{obs.}$) and derived rate constants [a] k_{12}, k_{21}, and k_{22} [as defined in equations (2) and (3)] for the stepwise reaction of $[Re(CO)_5X]$ with cyanide ion in aqueous methanol; ionic strength was maintained at 2.5×10^{-2} mol dm^{-3} with potassium nitrate. Mixed aqueous solvent compositions are cited by volume before mixing

			First stage					Second stage					
			10^2[KCN]/mol dm^{-3}					10^2[KCN]/mol dm^{-3}					
Complex	Solvent	T/K	1.0	1.5	2.0	2.5	k_{12}/dm^3 mol^{-1} s^{-1}	1.0	1.5	2.0	2.5	10^4k_{21}/s^{-1}	10^2k_{22}/dm^3 mol^{-1} s^{-1}
			$10^2k_{obs.}$/s^{-1}					$10^4k_{obs.}$/s^{-1}					
$[Re(CO)_5I]$	70% MeOH	293.2			1.09 [b]	1.40 [b]	0.55			1.07	1.32		
		298.2	1.17	1.81	2.5	2.8	1.14 ± 0.13	1.02	1.35	1.75	2.1	0.29 ± 0.03	0.72 ± 0.016
		303.3	2.1	3.5	4.4	5.1	2.00 ± 0.23	1.48	1.94	2.4	3.0	0.48 ± 0.10	1.00 ± 0.05
		308.1	2.5	4.9	6.7	10.3	4.99 ± 0.53	2.4	2.9	3.9	4.8	0.65 ± 0.28	1.63 ± 0.15
	50% MeOH	293.2	2.8	5.1	6.1	9.8	4.43 ± 0.72	1.95	2.6	3.5	4.0	0.59 ± 0.16	1.37 ± 0.08
			10^2[KCN]/mol dm^{-3}					10^2[KCN]/mol dm^{-3}					
			0.5	0.75	1.0	1.25		0.5	0.75	1.0	1.25		
$[ReBr(CO)_5]$	70% MeOH	293.2	2.6	3.4	4.1	6.4	4.9 ± 1.1	1.10	1.11	1.10	1.15	1.06 ± 0.03	(0.06 ± 0.04)
$[Re(CO)_5Cl]$	70% MeOH	293.2	2.1	2.6	3.5	4.8	3.6 ± 0.5	1.3	1.5	1.4	1.5	1.27 ± 0.10	(0.19 ± 0.11)

[a] Standard errors are cited. [b] Similar rate constants were obtained from runs at 301 nm (see text).

reaction of $[Re(CO)_5I]$ with cyanide ion. For the first stage, the activation parameters were computed from each individual $k_{obs.}/[CN^-]$ quotient. For the second stage, activation parameters were computed from k_{21} and k_{22} values which were themselves obtained at each temperature from plots of $k_{obs.}$ against cyanide concentration. The determined activation parameters, with an indication of their attendant uncertainties, are reported in Table 2.

Table 2

Activation parameters for the reaction of $[Re(CO)_5I]$ with cyanide ion in 70% methanol–water; the subscripts correspond with those given to the rate constants in equations (2) and (3) of the text. The uncertainties quoted are the standard errors of the parameters given

	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
First stage		
k_{12} term	85 ± 5	38 ± 17
Second stage		
k_{21} term	60 ± 7	−130 ± 25
k_{22} term	61 ± 12	−84 ± 46

The solubilities of $[Re(CO)_5I]$ and $[ReBr(CO)_5]$ are given in Table 3.

Table 3

Solubilities of rhenium pentacarbonyl halides in aqueous methanol at 293.2 K

Methanol composition (% v/v)	10^3 Solubility/mol dm^{-3}	
	$[Re(CO)_5I]$	$[ReBr(CO)_5]$
70	3.9	1.5
50	1.0	

DISCUSSION

The rate laws obtained, (2) and (3), suggest that the reactions of $[Re(CO)_5X]$ (X = Cl, Br, or I) with cyanide ion are bimolecular in mechanism. They presumably involve attack of the incoming cyanide at the rhenium atom. On the other hand, the reactions of the $[Re(CN)(CO)_4X]^-$ anions (X = Cl or Br) with cyanide ion appear to proceed by a predominantly dissociative mechanism. The reaction of the $[Re(CN)(CO)_4I]^-$ anion with cyanide ion appears to involve parallel dissociative and associative paths ($k_{21} \sim k_{22}[CN^-]$). This trend from associative attack for the first stage of a reaction with cyanide to more dissociative reactions of cyano-intermediates with further cyanide parallels the pattern observed for the reactions of a sexidentate Schiff-base complex of iron(II) [6] and of tris(2,2′-bipyridyl)iron(II) [7] with cyanide.

The activation entropies for the two stages of the reaction of $[Re(CO)_5I]$ with cyanide are not inconsistent with the above interpretation of the rate laws, providing one assumes that solvation and solvation changes play a dominant role in determining the activation entropies. The bimolecular reaction between two 1− species, $[Re(CN)(CO)_4I]^-$ and CN^-, would be expected to have a more negative activation entropy than a bimolecular reaction involving one uncharged species, *viz.* $[Re(CO)_5I]$ and CN^-. The latter reaction might, on electrostatic grounds, be expected to have an activation entropy in the region of zero.[8] The unexpectedly large negative activation entropy for the dissociative path (k_{21} term) in the reaction of the $[Re(CN)(CO)_4I]^-$ anion must be due to solvation changes consequent on charge and dipole distribution changes on forming the transition state. In view of the relatively large uncertainties in the determined activation entropies, it would seem unwise to attempt any more detailed interpretation.

The relative reactivities of the series $[M(CO)_5X]$ (M = Mn or Re; X = Cl, Br, or I) are generally in the order $[M(CO)_5Cl] > [MBr(CO)_5] > [M(CO)_5I]$. Such an order has been established for the reactions of $[Mn(CO)_5X]$ [9-11] and of $[Re(CO)_5X]$ [10,11] with PPh_3, and for carbon monoxide exchange at $[Re(CO)_5X]$. In comparing these trends with those observed for the present $[Re(CO)_5X] + CN^-$ reactions one must bear in mind that the above reactivity trend has been established for

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reactions of dissociative mechanism in very different solvents, *viz.* toluene, xylene, chloroform, carbon tetrachloride, and n-octane. Nevertheless the reactivity order for the dissociative path for reactions of $[Re(CN)(CO)_4X]^-$ anions with cyanide (in 70% methanol–water) is analogous (Table 1): $[Re(CN)(CO)_4Cl]^- > [ReBr(CN)(CO)_4]^- > [Re(CN)(CO)_4I]^-$. For the associative attack of cyanide at $[Re(CO)_5X]$ the order is similar: $[Re(CO)_5Cl] \sim [ReBr(CO)_5] > [Re(CO)_5I]$. The associative contribution to the reactions of the $[Re(CN)(CO)_4X]^-$ anions with cyanide ion when X = Cl or Br is too small for a reactivity order to be confidently stated.

Bimolecular reactions of low-spin iron(II) complexes with cyanide ion show a marked increase in rate as the proportion of the non-aqueous solvent increases in series of aqueous organic binary solvent mixtures. This trend can be attributed to the increase in chemical potential of the cyanide ion when this is transferred to a mixture richer in the organic compound.[12] The reaction of $[Re(CO)_5I]$ with cyanide goes more *slowly* in 70% than in 50% methanol–water (Table 1). This suggests that the change in chemical potential of $[Re(CO)_5I]$ in transferring this species from 50 to 70% methanol is of opposite sign to, and larger than, that for cyanide ion. The change in chemical potential for $[Re(CO)_5I]$ on transfer from 50 to 70% methanol is, from the solubility results in Table 3, -3.3 kJ mol^{-1} at 293.2 K. Sadly, the dearth of numerical thermochemical information on cyanide ion in solution prevents us from estimating the analogous change in chemical potential for this ion. In our analysis of the reaction kinetics for $[Fe(bipy)_3]^{2+} + CN^-$ in mixed aqueous media (bipy = 2,2′-bipyridyl)[12] we were able to use the assumption, based on close similarity of radii and of single-ion hydration enthalpies,[13] that cyanide and chloride ions have very similar transfer parameters and were thus able to use published Gibbs free energies of transfer of chloride ion from water into the appropriate water-rich mixtures. The situation with respect to free energies of transfer of chloride ion into methanol-rich mixtures[14–17] and into methanol itself,[16–19] leaves much to be desired. Thus reported values of $\delta_m\mu^\ominus(Cl^-)$ from water into methanol range from 3.0 to 8.57 kcal mol^{-1}.* It is therefore impossible for us to estimate $\delta_m\mu^\ominus(Cl^-)$ or $\delta_m\mu^\ominus(CN^-)$ for transfer from 50 to 70% methanol to a degree of precision which allows conclusive rationalisation of our kinetic results. Nonetheless our kinetic results are consistent with a value of $\delta_m\mu^\ominus(CN^-)$ of the order of magnitude suggested by the range of published data on $\delta_m\mu^\ominus(Cl^-)$ for water–methanol solvent mixtures. It does seem possible to rationalise reactivity trends here, in the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide,[12] and in the reaction of Fe^{3+}(aq) with thiocyanate[20] with some success in terms of chemical potentials and derived transfer functions.

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* 1 cal = 4.184 J.

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