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The Kinetics of the Reaction between Manganese Pentacarbonyl Bromide and β-Alanine

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SUMMARY

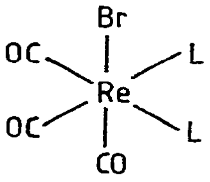
Manganese pentacarbonyl bromide reacts with β-alanine to give manganese tricarbonyl bis-(β-alanine) bromide. The kinetics of this reaction are described, the first step under thermal and the second under photochemical conditions. Rate constants in 50% aqueous methanol and in 50% aqueous dimethyl sulphoxide, and the activation enthalpy, entropy, and volume for the first step in 50% aqueous methanol are reported. The kinetic results suggest dissociative mechanisms for both stages, though there are some unusual features of the first step. Some rate constants for the reactions of manganese pentacarbonyl bromide with glycine and of rhenium pentacarbonyl bromide with β-alanine are also given.

INTRODUCTION

It has recently been established that rhenium pentacarbonyl bromide reactions with α- or β- alanine (1) to give the fac-tricarbonyl derivatives (2) containing monodentate amino-acid ligands bonded to the rhenium through nitrogen.[1] We have established an analogous reaction between manganese pentacarbonyl bromide and β-alanine, and report on the kinetics of this reaction.

$NH_2CH_2CH_2CO_2H$

(1)



(2); L = α- or β- alanine

RESULTS

Refluxing manganese pentacarbonyl bromide with an excess of β-alanine in dioxan for several hours gives a product which analyses correctly for the expected $Mn(CO)_3Br(\beta\text{-alanine})_2$. The very close similarity between the infra-red spectrum of this product and of fac-$Re(CO)_3Br(\alpha\text{-alanine})_2$ (cf. ref.1) indicates fac-geometry for the former. This stereochemical conclusion should be contrasted with reactions of $Mn(CO)_5Br$ with phosphorus ligands, where mer-geometry is more common for products $Mn(CO)_3Br(PR_3)_2$.[2]

The kinetics of the reaction of manganese pentacarbonyl bromide with β-alanine, and of some closely related reactions, were examined in aqueous methanol and, to a limited extent, in aqueous dimethyl sulphoxide. In both solvent mixtures the proportion of water was 50% by volume (before mixing). For all the reactions studied two kinetically distinct stages were observed, a first stage that proceeded in the dark and a second stage that only proceeded in light. In all our kinetic experiments β-alanine or glycine were present in large excess over the manganese pentacarbonyl bromide; under these conditions both stages followed first-order kinetics. Observed first-order rate constants for both stages, in 50% methanol at 298.5 K, are reported in Table 1. Results for reaction in 50% dimethyl sulphoxide at 298.5 K are given in Table 2, and for reaction of the rhenium compound, at 334.2 K, in Table 3. In all cases, except the first stage of the reaction of $Mn(CO)_5Br$ with β-alanine in 50% dimethyl sulphoxide, observed first-order rate constants are independent of β-alanine or glycine concentration, indicating the rate law (M = Mn or Re):

$$-d[M(CO)_5Br]/dt = \underline{k}_1[M(CO)_5Br]$$

For the reaction of $Mn(CO)_5Br$ with β-alanine in 50% dimethyl sulphoxide, the kinetics of the first stage (Table 2) indicate the rate law:

$$-d[Mn(CO)_5Br]/dt = \{\underline{k}_1 + \underline{k}_2[\beta\text{-alanine}]\}\,[Mn(CO)_5Br]$$

TABLE 1. Observed first-order rate constants for reaction of manganese pentacarbonyl bromide with β-alanine or glycine in 50% aqueous methanol at 298.5 K

[amino-acid]/mol dm^{-3}	0.012	0.062	0.094	0.130	0.187
Stage 1					
$10^5\underline{k}_{obs}$(β-alanine)/s^{-1}	9	12	11	10	10
$10^5\underline{k}_{obs}$(glycine)/s^{-1}	3.3	3.5		2.8	3.0
Stage 2					
$10^4\underline{k}_{obs}$(β-alanine)/s^{-1}	3.0				3.2
$10^4\underline{k}_{obs}$(glycine)/s^{-1}	2.7	2.2		3.1	3.5

TABLE 2. Observed first-order rate constants for reaction of manganese pentacarbonyl bromide with β-alanine in 50% aqueous dimethyl sulphoxide at 298.5 K

[β-alanine]/mol dm^{-3}	0.031	0.062	0.094	0.130	0.159
$10^3\underline{k}_{obs}$(stage 1)/s^{-1}	2.3	3.2	4.9	10.6	17.7
$10^4\underline{k}_{obs}$(stage 2)/s^{-1}		2.7	2.3	2.4	2.6

TABLE 3. Observed first-order rate constants for reaction of rhenium pentacarbonyl bromide with β-alanine in 50% aqueous methanol at 334.2 K

[β-alanine]/mol dm^{-3}	0.012	0.031	0.062	0.094	0.130	0.159	0.187
$10^4 \underline{k}_{obs}/s^{-1}$	1.8	1.8	1.4	1.8	1.6	1.4	1.5

The dependence of rate constant on temperature for the reaction of manganese pentacarbonyl bromide with β-alanine is reported in Table 4. A standard unweighted least-mean-squares treatment of these results leads to activation parameters $\Delta H^{\ddagger}$ = 121 ± 3 kJ mol^{-1} and $\Delta S^{\ddagger}$ = +84 ± 9 J K^{-1} mol^{-1} (at 298.5 K). First-order rate constants for this same reaction conducted at 1.01 and at 1.34 kbar, in 0.187 mol dm^{-3} β-alanine in 50% methanol at 298.5 K, are 2.9 and 4.2 x 10^{-4} s^{-1} respectively. These values, taken with the rate constant at atmospheric pressure under analogous conditions, indicate an activation volume ($\Delta V^{\ddagger}$) of −20 ± 5 ml^3 mol^{-1} for this reaction.

TABLE 4. Variation of observed first-order rate constants with temperature for the first stage of the reaction of manganese pentacarbonyl bromide with β-alanine in 50% aqueous methanol

T/K	298.5	307.8	316.4	325.4
$10^4 \underline{k}_{obs}/s^{-1}$	1.1	5.6	18.5	70

DISCUSSION

The rate law common to all the reactions studied, except the first stage in 50% dimethyl sulphoxide, indicates a dissociative mechanism. However the first-order rate constant for the reaction of $Mn(CO)_5Br$ with β-alanine is some three times larger than that for reaction with glycine.

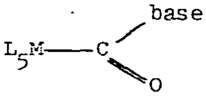
This small but significant difference indicates that the dissociative mechanisms cannot be entirely straightforward, a point which will be taken up again below. There are no data available for direct comparisons of rate constants for reactions of $Mn(CO)_5Br$ with other nucleophiles, since conditions, especially solvents used, differ. However values of k and $\Delta H^{\ddagger}$ for dissociative loss of carbon monoxide from $Mn(CO)_5Br$ here compare tolerably well with ranges of 10^{-4} to 10^{-3} s^{-1} for k (at 313 K) and of 108 to 127 kJ mol^{-1} for $\Delta H^{\ddagger}$ for substitution at this compound in a range of solvents.[3] They also, of course, compare satisfactorily with k and $\Delta H^{\ddagger}$ values for substitution by phosphorus bases at $Mn(CO)_5Br$, which also proceeds by a dissociative mechanism.[4] On the other hand rates for all these processes are much less than those for cyanide attack at $Mn(CO)_5Br$, which takes place by an associative mechanism.[5]

Slower substitution at rhenium than at manganese (Tables 1 and 3) is in accord with expectation. Again our rate constants for reaction of $Re(CO)_5Br$ with β-alanine compare satisfactorily with those reported for dissociative substitution and exchange at $Re(CO)_5Br$, which are between 5 and 15 x 10^{-5} s^{-1} in various solvents at 333 K.[6]

Rate constants for the second stages of the reactions of $Mn(CO)_5Br$ with β-alanine and with glycine are independent of the nature as well as of the concentration of the incoming amino-acid. Here we have entirely normal dissociative behaviour. Interestingly rate constants are also independent of solvent, being the same in 50% aqueous dimethyl sulphoxide as in 50% aqueous methanol. Photochemical activation and stretching of the Mn-CO bond is thus apparently dominant, with interactions between the leaving CO and its solvent environment of minor importance.

The rate law for the first stage of the reaction of $Mn(CO)_5Br$ with β-alanine in 50% dimethyl sulphoxide (see above) indicates parallel dissociative (solvolytic) and associative paths, with the latter dominant under our conditions. This difference between aqueous dimethyl sulphoxide and aqueous methanol may be ascribed to a markedly higher chemical potential of β-alanine in the former solvent mixture, which follows from the observed lower solubility. As implied above, the second stage in aqueous dimethyl sulphoxide has no associative character, being photodissociative.

The mechanistic picture for these reactions is therefore clear in all respects save one, the detailed path for the first stage of the reactions between $Mn(CO)_5Br$ and glycine or β-alanine in aqueous methanol. Three kinetic facts are not in accord with a simple dissociative ($\underline{I}_d$ or $\underline{D}$) rate-determining step. The difference in rate constants has already been pointed out. Values both of $\Delta S^{\ddagger}$ and of $\Delta V^{\ddagger}$ for the reaction with β-alanine also differ greatly from expectation for a dissociative process. Thus the $\Delta V^{\ddagger}$ value here contrasts greatly with reported values of +10 to + 15 $cm^3\ mol^{-1}$ for dissociative substitution at hexacarbonyls.[7] Also the values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ for this reaction of manganese pentacarbonyl bromide with β-alanine lie well away from the $\Delta S^{\ddagger}$ – $\Delta V^{\ddagger}$ correlation line established for substitution at "classical" transition metal centres.[8] We can only suggest that these kinetic anomalies may be ascribed in part to specific interactions between the $Mn(CO)_5Br$ and the amino-acids, and in part to drastic solvent reorganisation about the amino-acid as it goes from its solvated zwitterionic form in solution to the non-zwitterionic form in the pentacarbonyl manganese derivative. In respect of the former effect for $Mn(CO)_5Br$, such interactions involving nitrogen bases have recently been proposed to account for several observations in this area.[9] In our case the interactions could be as proposed (3), or could also involve some hydrogen-bonding to the carbonyl-oxygen. In order to explain our dependence of $\underline{k}_{obs}$ on nature but not on concentration of the amino-acid, it is necessary to propose that the $Mn(CO)_5Br$-amino-acid interaction is complete over the whole range of amino-acid concentrations covered, but that the strength of the interaction be dependent on the nature of the amino-acid involved. If this type of interaction exists, then the apparent $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ values may differ from expectation due to the consequences of this interaction. If solvation at the interacting amino-acid, or interaction between non-leaving carbonyl and amino-acid[10] is also important, then it becomes impossible to forecast activation parameters with any degree of confidence.



(3)

EXPERIMENTAL

Manganese tricarbonyl bis-β-alanine bromide was prepared by refluxing manganese pentacarbonyl bromide (Strem Chemicals) with the stoichiometric amount of β-alanine (Koch-Light) in dioxan for several hours. The crystals produced were filtered off, washed, and dried. They analysed satisfactorily for the stated product. Kinetic runs at atmospheric pressure were carried out in 10 mm silica cells in the thermostatted cell compartment of a Unicam SP800 or SP8-100 recording spectrophotometer. Kinetic runs at high pressures were carried out in a thermostatted pressure vessel; aliquots were ejected at intervals and reagent concentrations therein monitored on the SP800 spectrophotometer. Reagent concentrations are specified in the respective Table captions. Glycine was purchased from Koch-Light; rhenium pentacarbonyl bromide was kindly provided by Dr. J. G. Chambers. Methanol and dimethyl sulphoxide were purified by standard procedures;[11] binary aqueous solvent mixtures were made up according to volume proportions before mixing. All the runs whose rate constants are reported as stage 2 in Tables 1 and 2 were conducted simultaneously under identical conditions of illumination (sunlight).

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