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KINETICS OF LIGAND DISPLACEMENT FROM THE $Mn(acac)_3$ COMPLEX

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The rate of the displacement of the acetylacetonate ligand from the $Mn(acac)_3$ complex has been studied in methanol, in the presence of perchloric acid. Ion pair formation has been suggested. Mn(II) ions have been found to retard the rate of ligand displacement that has been attributed to the formation of a mixed valence complex.

Скорость замещения лиганда в комплексе Mn $(ацац)_3$ была исследована в метаноле и в присутствии надхлорной кислоты. Полагается образование ионной пары. Ионы Mn(II) замедляют скорость лигандного замещения, что приписывается образованию комплекса со смешанными валентностями.

INTRODUCTION

The ground state, $^5E_g(t_{2g}^3\ e_g)$, for Mn(III) in octahedral field, is subject to Jahn-Teller distortion. Owing to the presence of an odd number of e_g electrons, such distortion has been shown to be significant for many Mn(III) compounds /1/. The arrangement of the six oxygen atoms in $Mn(acac)_3$ does not show any large deviation from an octahedral arrangement /2/. A Jahn-Teller distortion would have bestowed stability on the $Mn(acac)_3$ complex. This lack of distortion in $Mn(acac)_3$ results in the inherent instability of this complex. As a consequence, ligand displacement is favored in protic solvents such as methanol. Although hydrogen bonding is possible in methanol, such solvation by hydrogen bonding would result in much of the solvation shell being removed in forming the activated complex.

We present here the kinetic results of the ligand displacement from the $Mn(acac)_3$ complex.

EXPERIMENTAL

Method. The $Mn(acac)_3$ complex, prepared by the standard method /3/, was dissolved in 10 ml of methanol, and the reaction was followed spectrophotometrically by monitoring the absorption band at 618 nm.

Product analysis. The reaction was carried out at 30 °C for 12 h. At the end of the reaction, the reaction mixture was shaken with 10% H_2SO_4 and ether, until the ether layer was light-yellow or colorless. The aqueous acid layer was extracted with ether, and the ether solution dried over Na_2SO_4. The solvent was distilled in vacuum, when acetylacetone was obtained in a yield of 60% (bp 139 °C, 750 mm). The product was further characterized by the monomethyl phenylhydrazone derivative (mp 98 °C). IR bands were obtained at 2920 (m), 1715 (s), 1620 (m), 1420 (m), 1350 (s), 1250 (s), 1000 (w), 950 (w) and 780 (m) cm^{-1}. UV analysis of the product in CCl_4 gave a sharp absorption band at 274 nm. The product of the reaction was thus confirmed to be acetylacetone.

RESULTS AND DISCUSSION

The reaction followed first order kinetics (Table 1).

The mechanism of the reaction involved ion pair formation via a short lived reactive intermediate species (Eq. 1), where the site for protonation would be the solvent. Ionization of the ion pair would follow, leading to the formation of acetylacetone (Eq. 2):

$$Mn^{III}(acac)_3 \xrightarrow[HClO_4]{\text{solvent}} [Mn^{III}(acac)_3\ (\text{solvent})\,H]^+\ ClO_4^- \qquad (1)$$

$$[Mn^{III}(acac)_3\ (\text{solvent})\,H]^+\ ClO_4^- \longrightarrow [Mn^{III}(acac)_2\ (\text{solvent})_2] + \\ + ClO_4^- + \text{acacH} + H^+ \qquad (2)$$

A shift in the absorption of the complex to longer wavelengths was observed, as a result of ion pair formation. This spectral shift from 618 nm to 630 nm would be due to the absorption of the ion pair formed in Eq. 1. Similar spectral changes have been observed due to ion pair formation in the case of some Co(II) complexes with halide ions /4/.

Table 1

Rate data for ligand displacement from the $Mn(acac)_3$ complex, and the effect of the addition of Mn(II) ions

$[Mn(acac)_3]$ (10^3 X M)	$[HClO_4]$ (M)	[Mn(II)] (10^3 X M)	10^5 X k_{obs} (s^{-1})
5.0	0.5	–	150.0
10.0	0.5	–	290.0
25.0	0.5	–	760.0
50.0	0.5	–	1500.0
10.0	0.1	–	28.0
10.0	0.8	–	220.0
10.0	1.0	–	290.0
5.0	0.5	5.0	112.0
5.0	0.5	10.0	35.0
5.0	0.5	30.0	15.0

μ = 1.0 M; temp. = 30.0±0.1 °C; all values of rate constants were the average of two or more experiments, with agreement being ±1.5% or better

Effect of Mn(II) ions. The addition of Mn(II) ions caused a retardation in the rate of the reaction (Table 1). This retarding effect can be attributed to the formation of a mixed valence complex, $Mn^{III}(acac)_xMn^{II}$, which may not undergo homolysis. The absorption band of the Mn(II) species in solution has been ascribed to a d–d transition, assigned as $^5B_{1g} \rightarrow {}^5E_g$, assuming D_{4h} symmetry /1/. Undoubtedly, Mn(II) affects this transition in the Mn(III) species. Direct evidence for the $Mn^{III}Mn^{II}$ mixed valence complex can be obtained by an examination of the ESR spectrum in a manner similar to that employed in the Cu^ICu^{II} mixed valence complex /5/. We have examined the ESR spectrum for evidence of a mixed valence complex, and it might be pertinent to make two significant observations:

(a) no further splitting of the Mn(II) sextet could be observed in the presence of excess Mn(III);

(b) a slight line broadening leads to a diminution of the peak-to-peak heights of the derivative signal of Mn(II). However, such line broadening may arise in various ways, such as exchange due to bimolecular reactions between Mn(II) and Mn(III).

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