Inorganica Chimica Acta, 37 (1979) 85–87
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Kinetics of Nucleophilic Attack on Coordinated Organic Moieties.
Part 10. Addition of N,N-dimethylaniline to Tricarbonyl(cyclohexadienyl)ruthenium Cation[a]

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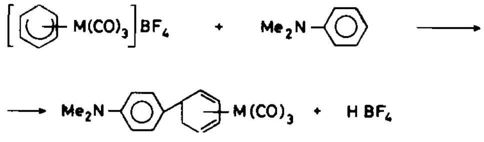
Received March 13, 1979

A detailed kinetic study has been made of the addition of N,N-dimethylaniline to the cations $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ *(M = Fe, Ru) in nitromethane. The rate law Rate =* $k[\text{complex}][Me_2NC_6H_5]$ *is observed with both metals, suggesting a common mechanism involving direct addition at the dienyl rings. The greater rapidity of the iron reaction* (k_{Fe}/k_{Ru} *= 48 at 40 °C) arises almost entirely from its lower enthalpy of activation* ($\Delta H^{\ddagger}_{Fe} = 53.3 \pm 1.3$ *kJ mol*$^{-1}$, $\Delta H^{\ddagger}_{Ru} = 62.8 \pm 0.7$ *kJ mol*$^{-1}$).

Introduction

We recently reported [1] the preparation of derivatives of the type (I) formed via reaction between $[(\eta^5\text{-}C_6H_7)M(CO)_3]BF_4$ (M = Fe, Ru, Os) and N,N-dimethylaniline (eqn. 1). These reactions provided a further example of the synthetic utility of employing organometallic cations as electrophiles towards aromatic substrates. A detailed kinetic study was carried out on the iron system in acetonitrile solvent, while preliminary kinetic data for the M = Ru, Os complexes indicated that the electrophilicity of the dienyl ligand decreases in the order Fe > Os > Ru (41:3.6:1). However, this unique comparison rested on the assumption of a common mechanism down the triad.



(1)

This paper now reports detailed kinetic studies for reaction (1, M = Ru) in nitromethane. The ruthenium cation $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]^+$ decomposes in acetonitrile preventing study in this solvent. Therefore in order to facilitate comparison the analogous iron cation has been more fully investigated in nitromethane. Activation parameters determined for both M = Fe and Ru complexes in this common solvent throw some light on the source of their different electrophilicities.

Experimental

Materials

The complexes $[(\eta^5\text{-}C_7H_7)M(CO)_3]BF_4$ (M = Fe, Ru) were synthesised and purified by published

TABLE I. Kinetic Results for Reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]BF_4$[a] with N,N-dimethylaniline in CH_3NO_2.

Temp./°C	$10^2[Me_2NC_6H_5]$/mol dm^{-3}	$10^4\ k_{obs}/s^{-1}$	$10^2\ k$/mol^{-1} dm^3 s^{-1}
20.0	2.02	2.80	1.43 ± 0.02
20.0	3.01	4.21	
20.0	4.03	5.80	
20.0	5.50	7.76	
30.0	0.504		2.06
35.0	0.504		3.20
40.0	0.504		4.42
45.0	0.504		6.06
50.0	0.504		8.68
55.0	0.504		11.2

[a]For 20 °C runs [Fe] = 3.0×10^{-3} mol dm^{-3}. For all other temperatures [Fe] = 5.04×10^{-3} mol dm^{-3}.

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[a]Part 9. G. R. John, L. A. P. Kane-Maguire, T. Odiaka and A. Salzer, *J. Chem. Soc. Dalton,* in press.

procedures [2, 3]. Their purity was checked by elemental analyses and i.r. spectroscopy.

Nitromethane solvent (BDH) was distilled under an atmosphere of nitrogen and stored over molecular sieves (grade 3A). It was deoxygenated by passing through a stream of nitrogen for 20 min immediately prior to use. N,N-dimethylaniline was distilled at reduced pressure from over KOH pellets and stored under nitrogen in the dark.

Kinetic Studies

Reactions (1, M = Fe, Ru) were monitored by i.r. spectroscopy using techniques described [1] previously. The disappearance of the longest wavelength band located at *ca.* 2110 cm^{-1} for both $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ cations was followed using a Perkin-Elmer 257 spectrophotometer.

The majority of the kinetic runs were carried out under pseudo-first-order conditions using a large excess of N,N-dimethylaniline. k_{obs} values were calculated from the slopes of plots of log A_t *versus* time, which were generally linear for at least 80% completion of reaction.

However because of the rapidity of the Fe reactions at 30 °C or above, it was more convenient to study these latter processes under equimolar conditions ($[Fe] = [Me_2NC_6H_5] = 5.04 \times 10^{-3}$ mol dm^{-3}). In these cases the second-order rate constants k were obtained directly from the slopes of plots of x/a (a – x) *versus* time (where a = initial concentration of dienyl salt, and x = concentration of product at time t). Such plots were linear for at least 75% completion of reaction.

Activation enthalpies were calculated from the slopes of Arrhenius plots of log k *versus* 1/T using a least squares method. The errors quoted are the standard errors of estimation from these analyses. Entropies of activation were calculated using second-order rate constants.

TABLE II. Kinetic Results for Reaction of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$ with N,N-dimethylaniline in CH_3NO_2. $[Ru] = 3.02 \times 10^{-3}$ mol dm^{-3}.

Temp./°C	10 $[Me_2NC_6H_5]$/mol dm^{-3}	10^4 k_{obs}/s^{-1}
30.0	2.02	0.827
35.0	2.02	1.19
40.0	0.301	0.269
40.0	0.601	0.506
40.0	1.03	0.871
40.0	2.02	1.89
40.0	3.01	2.80
40.0	4.04	3.68
45.0	2.02	2.80
50.0	2.02	3.97
55.0	2.02	5.86

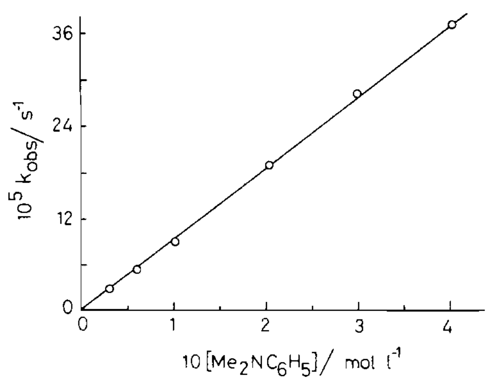


Fig. 1. Plot of k_{obs} *versus* $[Me_2NC_6H_5]$ for the reaction of $[(\eta^5\text{-}C_6H_7)Ru(CO)_3]BF_4$ with N,N-dimethylaniline in CH_3NO_2 at 40.0 °C.

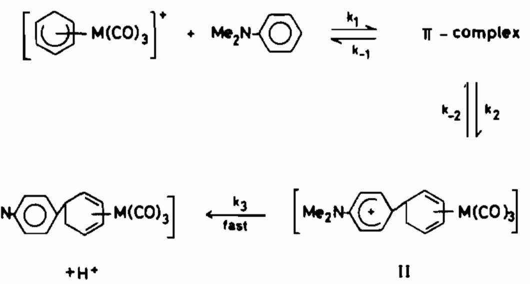
Results and Discussion

Kinetic results for reactions (1; M = Fe, Ru) in nitromethane are summarised in Tables I and II. With both metals the second-order rate law (2) is seen to be obeyed (*e.g.* Fig. 1). This rate law is the same as that found previously [1] for the iron complex in acetonitrile solvent, and supports a common mechanism for all reactions. It is consistent with the general scheme below in which either (i) π-complex formation is rate-determining (*i.e.* $k_{obs} = k_1[Me_2NC_6H_5]$), or (ii) there is no significant contribution from a π-complex intermediate and formation of the Wheland-type σ-complex (II) is rate-limiting.

$$\begin{aligned}\text{Rate} &= k_{obs}[M] \\ &= k[M][Me_2NC_6H_5] \qquad (2)\end{aligned}$$

TABLE III. Rate and Activation Parameters for Reaction of $[(\eta^5\text{-}C_6H_7)M(CO)_3]BF_4$ (M = Fe, Ru) with N,N-dimethylaniline in CH_3NO_2.

Metal	10^4 $k_{40\,°C}$/mol^{-1} dm^3 s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Fe	442	53.3 ± 1.3	–102 ± 4
Ru	9.29	62.8 ± 0.7	–103 ± 3



A similar common mechanism has recently been suggested [4] for the analogous reactions of $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe, Ru) with the heterocyclic aromatic substrate pyrrole. In contrast, with indole different pathways are followed by the iron and ruthenium complexes, the kinetic data indicating [5] the presence of an intermediate (perhaps a π-complex) in the ruthenium case. Failure to detect any intermediate spectroscopically or kinetically in reactions (1; M = Fe, Ru) supports direct addition of N,N-dimethylaniline to the dienyl rings of both cations.

Table III compares rate and activation parameters for the iron and ruthenium reactions in nitromethane. At 40 °C the iron cation reacts *ca.* 48 times faster with N,N-dimethylaniline than does the analogous ruthenium complex (the k_{Fe}/k_{Ru} ratio varies between 39 at 55 °C and 50 at 35 °C). These differences in reactivity are seen to arise almost entirely from the considerably lower $\Delta H^{\ddagger}$ value for the iron complex. Both compounds exhibit large negative $\Delta S^{\ddagger}$ values of *ca.* −102 J K^{-1} mol^{-1}, as expected for the common associative mechanism in the Scheme. The limited significance of solvation effects is emphasised by the very similar activation parameters previously found [1] for the iron complex in acetonitrile solvent ($\Delta H^{\ddagger}$ = 55.8 ± 0.8 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −99 ± 10 J K^{-1} mol^{-1}).

Since steric effects are expected to be similar for the iron and ruthenium cations if addition occurs directly on the dienyl rings, the lower $\Delta H^{\ddagger}$ and faster rates for the iron complex may simply reflect the different electronic influences of the $M(CO)_3$ moieties on the π-hydrocarbon ligands. This suggests that $Ru(CO)_3$ is a more effective overall electron donor than $Fe(CO)_3$ resulting in a less positive dienyl ring. This conclusion is consistent with the observation [6] that while methoxide attack on $[(\eta^5\text{-}C_6H_7)\text{-}Fe(CO)_3]BF_4$ appears to occur directly on the dienyl group, with the related ruthenium cation the kinetically favoured site for initial attack is a carbonyl ligand.

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