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Kinetics of Nucleophilic Attack on Coordinated Organic Moieties. Part 13. Addition of N,N-dimethylaniline to Tricarbonyl(tropylium)chromium Tetrafluoroborate [1]

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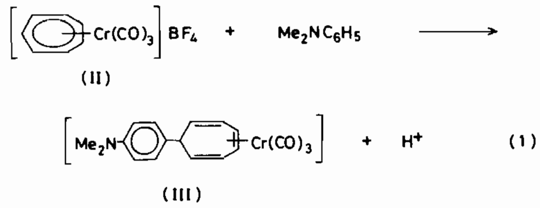
A kinetic study of the reaction of $[(\eta\text{-}C_7H_7)\text{-}Cr(CO)_3]BF_4$ *(II) with N,N-dimethylaniline in* CH_3NO_2 *to yield tricarbonyl[7-(4-dimethylaminophenyl)cyclohepta-1,3,5-triene]chromium has revealed the two-term rate law, Rate =* $k_a[complex][Me_2NC_6H_5]^2 + k_b[complex][Me_2NC_6H_5]$. *This rate law is consistent with a mechanism involving electrophilic attack* (k_1, k_{-1}) *by (II) on N,N-dimethylaniline to give a steady-state concentration of a Wheland σ-complex intermediate, followed by competing amine* (k_2)*- and solvent* (k_3)*-assisted proton removal to produce the product. Assuming this mechanism, the parameters* k_a *and* k_b *refer to* $k_1k_2/(k_{-1} + k_3)$ *and* $k_1k_3/(k_{-1} + k_3)$*, respectively. The results are compared with the simpler kinetic behaviour previously observed for the related reactions of the dienyl cations* $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ *(M = Fe, Ru).*

Introduction

The use of dienyl cations of the type $[(\eta^5\text{-dienyl})M(CO)_3]^+$ (I) as electrophiles towards heterocyclic aromatic species and activated arenes has recently been shown to provide novel routes to diene-substituted aromatic species [2–6]. Kinetic investigations of the reactions of (I; dienyl = C_6H_7; M = Fe, Ru) with heterocyclic aromatic substrates [7, 8] and N,N-dimethylaniline [6, 9], and of acyclic dienyl iron cations with di- and tri-methoxybenzenes [5] indicate that these reactions are related to aromatic substitutions with more normal electrophiles.

From preliminary studies [6, 10] with other $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ cations it appears that such reactions may have wide synthetic applications. For example, we recently reported [6] that reaction (1) proceeds with good yield in nitromethane. In order to further elucidate the nature of such processes we report here kinetic studies of reaction (1).



Experimental

Materials

The complex $[(\eta\text{-}C_7H_7)Cr(CO)_3]BF_4$ (II) was prepared and purified using published procedures [11]. *Anal.* Found: C, 38.5; H, 2.7; Calc. for $C_{10}H_7BF_4CrO_3$: C, 38.2; H, 2.2%. The nitromethane solvent was purified by distillation under nitrogen and stored over molecular sieves (grade 3A). N,N-dimethylaniline (Aldrich Chemical Co. Ltd.) was distilled at reduced pressure before storing under nitrogen in the dark.

The product (III), tricarbonyl[7-(4-dimethylaminophenyl)cyclohepta-1,3,5-triene]chromium has been previously isolated and fully characterised from analyses, i.r., ^1H n.m.r., and field-desorption mass spectra [6].

Kinetic Studies

Solutions of the reagents ([Cr] = 6×10^{-3} mol dm^{-3}; $[Me_2NC_6H_5]$ = 0.10–1.1 mol dm^{-3}) were freshly prepared in volumetric flasks (5 or 10 cm^3) and sealed under nitrogen with suba seals. The flasks were covered with alumina foil to exclude light and placed in a thermostatted bath at the desired temperature (±0.1 °C). Samples were then withdrawn via syringe at appropriate intervals, and their i.r. spectra recorded over the region 2150–1800 cm^{-1} on a Perkin Elmer 257 spectrophotometer using matched 0.5 mm NaCl liquid cells.

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The reactions were monitored by following the disappearance of the strong carbonyl band of the original cation (II) at 2065 cm^{-1}. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log A_t *vs.* time, where A_t is the absorbance at time t. Such plots were linear for at least two half-lives and usually for three half-lives.

Values of the slopes (k_a) and intercepts (k_b) from plots of $k_{obs}/[Me_2NC_6H_5]$ *vs.* $[Me_2NC_6H_5]$ were obtained using a least squares programme. In independent experiments no background reaction between the solvent and (II) was observed after 24 hr at 45 °C.

Results and Discussion

Reaction (1) proceeds to completion in CH_3NO_2 as evidenced both by ^1H n.m.r. spectroscopy and the complete disappearance of the original i.r. carbonyl bands of cation (II) at 2065 and 2015 cm^{-1} and the growth of strong bands for product (III) at 1970, 1900, and 1870 cm^{-1}. Kinetic results for this process at various temperatures and nucleophile concentrations are summarised in Table I. The two-term rate law (2) is seen

$$\text{Rate} = k_{obs}[\text{complex}]$$

$$k_{obs} = k_a[Me_2NC_6H_5]^2 + k_b[Me_2NC_6H_5] \qquad (2)$$

to be obeyed at each temperature, since plots of $k_{obs}/[Me_2NC_6H_5]$ *vs.* $[Me_2NC_6H_5]$ are linear with a non-zero intercept (*e.g.* Fig. 1). Values for the parameters k_a and k_b, obtained from a least-squares treatment of such plots, are listed in Table II, together with their associated standard deviations.

TABLE I. Rate Constants for the Reaction of N,N-dimethylaniline with $[(\eta\text{-}C_7H_7)Cr(CO)_3]BF_4$ in Nitromethane.

Temp. (°C)	$[Me_2NC_6H_5]$/mol dm^{-3}	10^4 k_{obs}/s^{-1}
23.7	0.10	0.049
	0.50	0.880
	0.70	1.37
	0.90	2.45
	1.00	2.92
	1.10	3.22
35.4	0.10	0.110
	0.50	1.52
	0.70	2.93
	0.90	4.59
	1.00	5.71
40.8	0.10	0.147
	0.50	2.25
	0.70	3.54
	0.90	5.76
	1.00	6.77

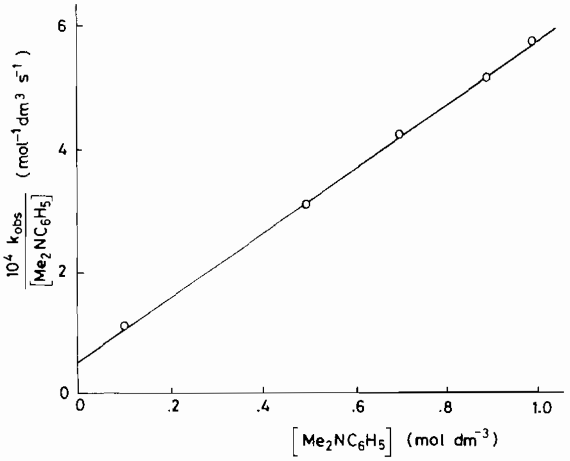


Fig. 1. Plot of $k_{obs}/[Me_2NC_6H_5]$ *vs.* $[Me_2NC_6H_5]$ for reaction of $[(\eta\text{-}C_7H_7)Cr(CO)_3]BF_4$ with $Me_2NC_6H_5$ in CH_3NO_2 at 35.4 °C.

Rate law (2) contrasts with the first-order dependence on $[Me_2NC_6H_5]$ previously found [6, 9] for the analogous reactions of $Me_2NC_6H_5$ with the dienyl cations $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (IV; M = Fe, Ru) (eqn. 3, ArH = $Me_2NC_6H_5$). Simple kinetic expressions of

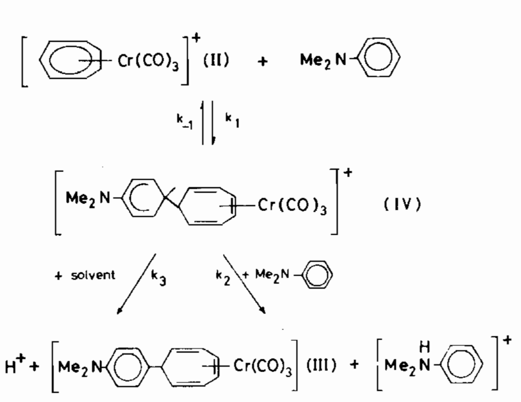
$$k_{obs} = k[ArH] \qquad (3)$$

the form (3) have also been previously observed for related reactions of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ with the heterocyclic aromatic species pyrrole [8], indole [7], and furan [8]. The more complex behaviour of the chromium cation (II) with $Me_2NC_6H_5$ may be rationalised by the mechanism shown in Scheme 1.

In this proposed mechanism, electrophilic attack by (II) on the $Me_2NC_6H_5$ substrate to form the Wheland σ-complex (IV) is followed by competing

TABLE II. Values of k_a and k_b at Various Temperatures for Reaction (1).

Temp. (°C)	10^4k_a/mol^{-2} dm^6 s^{-1}	10^5k_b/mol^{-1} dm^3 s^{-1}	k_a/k_b/mol^{-1} dm^3
23.7	2.52 (0.18)	3.26 (1.40)	7.7 (3.3)
35.4	5.10 (0.08)	5.60 (0.59)	9.1 (1.0)
40.8	5.82 (0.40)	11.1 (2.8)	5.2 (1.3)



Scheme 1

amine (k_2)- and solvent (k_3)-assisted proton removal, to yield the product. Assuming a steady-state concentration for intermediate (IV), the rate expression (4) is expected for Scheme 1.

$$k_{obs} = \frac{k_1k_2[Me_2NC_6H_5]^2 + k_1k_3[Me_2NC_6H_5]}{k_{-1} + k_3 + k_2[Me_2NC_6H_5]} \qquad (4)$$

Provided $k_2[Me_2NC_6H_5] \ll k_{-1} + k_3$, this equation simplifies to (5), which has the same form as the observed rate law (2). Also consistent

$$k_{obs} = \frac{k_1k_2[Me_2NC_6H_5]^2}{k_{-1} + k_3} + \frac{k_1k_3[Me_2NC_6H_5]}{k_{-1} + k_3} \qquad (5)$$

with this steady-state mechanism is the failure to detect any i.r. bands assignable to the intermediate (IV) during reaction (1), the only peaks observed being those due to the starting complex and final product.

Assuming the mechanism in Scheme 1, the calculated parameters k_a and k_b (Table II) may be equated with $k_1k_2/(k_{-1} + k_3)$ and $k_1k_3/(k_{-1} + k_3)$, respectively. Thus, the k_a/k_b ratios in Table II correspond to k_2/k_3, *i.e.* the ratio of the rate constants for amine-assisted and solvent-assisted (or spontaneous) proton removal. Because of the complex nature of k_a and k_b, their associated activation parameters have not been calculated. However, the apparent decrease in the k_2/k_3 ratio with increase in temperature (Table II) suggests a higher enthalpy of activation for the solvent- or non-assisted proton removal path (k_3) compared with the amine-assisted (k_2) route.

An alternative treatment of the mechanism in Scheme 1, assuming the rapid pre-equilibrium (K_1) formation of intermediate (IV) followed by slow proton removal (k_2 and k_3), leads to the general rate expression (6). This equation is also

$$k_{obs} = \frac{K_1k_2[Me_2NC_6H_5]^2 + K_1k_3[Me_2NC_6H_5]}{1 + K_1[Me_2NC_6H_5]} \qquad (6)$$

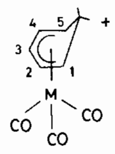
consistent with the observed rate law (2), provided $K_1[Me_2NC_6H_5] \ll 1$ at all amine concentrations employed. In this case, the parameters k_a and k_b may be equated with K_1k_2 and K_1k_3 respectively. However, the k_a/k_b ratios in Table II again correspond to k_2/k_3.

Although the rate law (2) observed here for reaction (1) contrasts sharply with the kinetic behaviour previously observed [6, 9] for the related reactions with the dienyl cations $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (I; M = Fe, Ru), each of these processes may in fact be accommodated by the general mechanism outlined in Scheme 1. Assuming a common steady-state mechanism, the absence of a second-order term in $[Me_2NC_6H_5]$ in the rate law for the Fe and Ru cations can be understood provided $k_2[Me_2NC_6H_5] \gg k_{-1} + k_3$ at all amine concentrations employed. Under this condition, the general rate law (4) collapses to eqn. (7),

$$k_{obs} = k_1[Me_2NC_6H_5] + k_1k_3/k_2 \qquad (7)$$

which conforms with the observed rate law (3) providing the term k_1k_3/k_2 is very small. Alternatively, as suggested previously [5, 8], rate law (3) may hold for cations (I) because the final proton removal steps (k_2 and/or k_3) are much faster than the formation of the Wheland σ-complex intermediate.

Nevertheless, it is possible that the observed differences between the chromium cation (II) and the Fe and Ru complexes (I) may reflect fundamental differences in mechanism. For reactions involving nucleophilic attack at the π-hydrocarbon ligands, one might anticipate some mechanistic differences in view of the different stereochemical requirements. While the tropylium ring in (II) is flat, the cyclohexadienyl ring in (I)



(I)

contains a methylene group bent above the plane of the other five carbon atoms. Thus, π-complex formation between the π-hydrocarbon and a suitable aromatic species such as N,N-dimethylaniline should be sterically more favoured for cation (II). Similarly, whereas nucleophilic attack by the N atom of N,N-dimethylaniline on the C(1) (or (C5)) position of (I) seems highly unlikely on steric grounds, the possibility of some contribution from this alternative pathway must be considered for cation (II). Aniline and ring-substituted anilines are believed [12] to form adducts with (II) in which they are attached to the tropylium ring *via* their N centre (similar adducts are also known [13] for (I, M = Fe). However, no spectroscopic evidence was found for the intermediacy of such an adduct in reaction (1). Furthermore, it is difficult to envisage a mechanism involving such an

N-bonded adduct which would lead to the final C-substituted N,N-dimethylaniline product (III), and yet give the observed rate law (2).

Acknowledgments

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