Mechanisms of Organometallic Reactions. Part I. Kinetics of the Reaction of Acetonitrile with Tricarbonyl(tropylium) Cations of Metals in Group VI

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The kinetics of removal of the tropylium ligand from the complexes $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, or W) have been studied using acetonitrile as nucleophile. A rate law of the form Rate = k[Complex][MeCN] is obeyed suggesting an S_N2 displacement mechanism. The ease of displacement of the tropylium ligand decreases markedly in the order Mo > W ≫ Cr, the relative rates being largely enthalpy controlled ($\Delta H^\ddagger$ = 10·5, 15·0, and 24·2 kcal mol^{-1} for M = Mo, W, and Cr respectively).

As part of a series of studies[1] on the mechanisms of nucleophilic attack on co-ordinated organic molecules, we recently attempted to study the addition of β-diketone compounds to the tropylium complex $[(C_7H_7)Cr(CO)_3]BF_4$ in acetonitrile as solvent. Rather than yielding the expected[2] ring-substituted cycloheptatriene complex, attack by acetonitrile at the chromium atom was observed. The tropylium group was displaced giving rise to a complex mixture of products including the complex *cis*-$[Cr(MeCN)_3(CO)_3]$. It therefore seemed interesting to investigate the reaction of acetonitrile alone with the substrate $[(C_7H_7)Cr(CO)_3]BF_4$, since this would constitute the first study of the manner and ease of displacement of the tropylium ion from metal complexes.

This paper reports the kinetics of reaction (1) (M = Cr, Mo, or W) together with limited data for other nitriles.

$$[(C_7H_7)M(CO)_3]BF_4 + 3MeCN \longrightarrow cis\text{-}[M(MeCN)_3(CO)_3] + (C_7H_7)BF_4 \quad (1)$$

The reactions have been shown to be kinetically second order, and are interpreted in terms of S_N2 displacement of $C_7H_7^+$ from the complex by MeCN ligands. These results therefore provide a useful model for the kinetic and activation parameters to be expected for reactions involving metal–nucleophile bond formation, and should prove useful in elucidating the mechanism of nucleophilic ring addition in $[(C_7H_7)M(CO)_3]BF_4$ systems.

EXPERIMENTAL

The tropylium complexes were prepared by published methods[3] and recrystallised from acetone. Their purity was checked by analysis {Found: C, 38·1; H, 2·2. $[(C_7H_7)Cr(CO)_3]BF_4$ requires C, 38·2; H, 2·2. Found: C, 33·7; H, 2·4. $[(C_7H_7)Mo(CO)_3]BF_4$ requires C, 33·6; H, 2·0. Found: C, 25·9; H, 1·5. $[(C_7H_7)W(CO)_3]BF_4$ requires C, 26·7; H, 1·6%} and by comparison of their i.r.

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[1] L. A. P. Kane-Maguire, *J. Chem. Soc. (A)*, **1971**, 1602.
[2] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3479.
[3] J. D. Munro and P. L. Pauson, *Proc. Chem. Soc.*, 1959, 267.

spectra with published data.[2] The $[(MeCN)_3M(CO)_3]$ species were isolated following the procedure of Tate *et al.*[4] All solvents for kinetic experiments were freshly distilled, and the acetonitrile was stored over molecular sieves. The solvents were deoxygenated by passing a stream of nitrogen through them for 0·5 h immediately prior to use.

Kinetic Determinations.—Runs were carried out in volumetric flasks (10 cm^3) which were wrapped in aluminium foil. The acetonitrile or appropriate fresh solvent mixture was thermostatted at the desired temperature ($\pm$0·1 °C), and then the solid complex $[(C_7H_7)M(CO)_3]BF_4$ was added to give final [M] *ca.* 3 × 10^{-3}M. The mixture was vigorously shaken to hasten dissolution and the flask sealed under an atmosphere of nitrogen with a serum cap. After 10 min equilibration samples were withdrawn periodically by syringe and their i.r. spectra recorded between 2100 and 1770 cm^{-1} using a Perkin-Elmer 257 spectrophotometer. Matched 0·5 mm NaCl cells were employed. Tests showed that no significant decomposition occurred in the i.r. beam.

The reactions were followed by monitoring the disappearance of the strong carbonyl band of the starting complex at 2070 cm^{-1}. This band was shown to obey Beer's law over the concentration range of interest. The only product peaks observed during the reaction were assigned to the species $[M(MeCN)_x(CO)_{6-x}]$ (x = 1—3) from their published spectra.[5,6] The peaks were well separated from the 2070 cm^{-1} substrate band. The reactions proceeded to completion and first-order rate constants were obtained from plots of log A_t against time, where A_t is the absorbance at time t of the reaction solution at 2070 cm^{-1}.

RESULTS

All reactions were carried out under pseudo-first-order conditions using a large excess of nucleophile. Good first-order plots were generally obtained for up to 80% completion of reaction. Kinetic (k_{obs}) data for reaction (1) in MeCN are summarised in Table 1, together with second-order rate constants calculated assuming $k_2 = k_{obs}$/[MeCN].

TABLE 1

Kinetic data for reaction of the complex $[(C_7H_7)M(CO)_3]BF_4$ with MeCN (19·1M)

Complex	Temp. / °C	10^5k_{obs} / s^{-1}	10^6k_2 / l mol^{-1} s^{-1}
$[(C_7H_7)Cr(CO_3)]BF_4$	50·6	0·654	0·342
	55·2	0·920	0·482
	65·0	3·18	1·66
	65·4	3·50	1·83
	70·4	6·40	3·36
$[(C_7H_7)Mo(CO)_3]BF_4$	25·3	14·0	7·33
	30·0	19·7	10·3
	35·5	26·0	13·6
	45·5	42·8	22·4
$[(C_7H_7)W(CO)_3]BF_4$	27·0	2·87	1·50
	35·7	6·43	3·37
	41·5	11·1	5·81
	50·4	18·4	9·63

Most of the rate constants were the average of duplicate or triplicate determinations (average reproducibility $\pm$5%). $\Delta H^\ddagger$ Values (Table 2) were obtained from gradients of Arrhenius plots, while $\Delta S^\ddagger$ data were calculated from standard equations.[7] Comparison with kinetic data for other nitriles is made in Table 3. The Figure shows the linear dependence of k_{obs} on [MeCN] for the reaction of acetonitrile with the complex $[(C_7H_7)Mo(CO)_3]BF_4$ in 1,2-dichloroethane as solvent, indicating the rate law (2).

TABLE 2

Activation parameters for reaction of the complex $[(C_7H_7)M(CO)_3]BF_4$ with MeCN

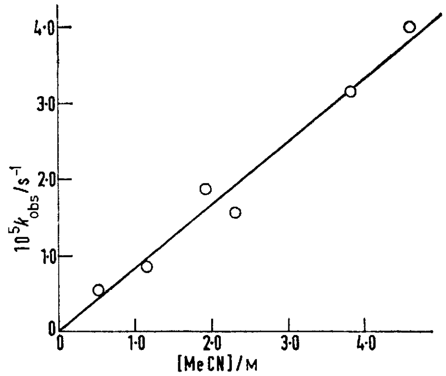
M	10^4k_{obs} (50·5 °C) / s^{-1}	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}
Cr	0·065	24·2	−10
Mo	5·50 [a]	10·5	−40
W	1·84	15·0	−30

[a] Extrapolated from E_a plot.

TABLE 3

Rates of reaction of the complex $[(C_7H_7)Cr(CO)_3]BF_4$ with various nitriles (temp. = 70·4 °C)

Nucleophile	[Nucleophile] / M	10^5k_{obs} / s^{-1}	10^6k_2 / l mol^{-1} s^{-1}
MeCN	19·1	6·40	3·36
EtCN	14·2	10·4	7·32
PhCN	9·7	6·58	6·80



Dependence of k_{obs} on [MeCN] for the reaction of MeCN with the complex $[(C_7H_7)Mo(CO)_3]BF_4$ in dichloroethane at 45·5 °C

$$\text{Rate} = k_2[\text{Complex}][\text{MeCN}] \qquad (2)$$

Since the plot passes through the origin, no measurable decomposition of the complex occurs in dichloroethane.

DISCUSSION

Nature of the Reaction.—I.r. spectral changes during the reaction of MeCN with the complex $[(C_7H_7)M(CO)_3]BF_4$ were consistent with equation (1), showing the formation of *cis*-$[(MeCN)_3M(CO)_3]$ as the sole product (strong carbonyl group bands at 1920 and 1800 cm^{-1}), provided the solvent was rigorously deoxygenated and care was taken not to admit air through the serum cap while withdrawing samples. However, in some of the runs

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[4] D. P. Tate, W. R. Knipple, and J. M. Augl, *Inorg. Chem.*, 1962, **1**, 433.

[5] G. R. Dobson, M. F. A. El Sayed, I. W. Stolz, and R. K. Sheline, *Inorg. Chem.*, 1962, **1**, 526.

[6] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, 1963, **2**, 323.

[7] 'Techniques of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1961, vol. VIII, part 1, p. 201.

the primary tri(carbonyl) product was observed to convert slowly to mixtures of tetracarbonyl (peaks at 1910, 1880, and 1840 cm^{-1}) and pentacarbonyl species (peak at 1945 cm^{-1}). These latter observations suggested equilibria of the type (3), which have previously been

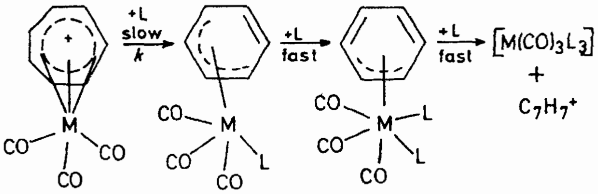
$$[(MeCN)_3M(CO)_3] \rightleftharpoons [(MeCN)_2M(CO)_4] \rightleftharpoons [(MeCN)M(CO)_5] \quad (3)$$

reported by Dobson *et al.*[5] in $[(MeCN)_xM(CO)_{6-x}]$ (x = 0—3, M = Cr, Mo, or W) systems. However, equilibria (3) were believed [5] to arise because of the presence of free CO, whereas no free CO is expected in the present systems.

Our observation of the occasional formation of pentacarbonyl species can be explained from independent experiments with freshly prepared $[(MeCN)_3Mo(CO)_3]$. Solutions of this pure species in MeCN under strictly anaerobic conditions were found to remain unchanged after 1 day at room temperature. However, the introduction of oxygen caused the $[(MeCN)_3Mo(CO)_3]$ complex to slowly convert to mixtures of the tetra- and pentacarbonyl complexes. Thus, the slow appearance of these latter species in some of our kinetic runs probably results from the gradual ingress of oxygen through the serum cap. The mechanism of conversion process (3) is uncertain, but it is interesting that similar behaviour has been described [8] for the corresponding tris(pyridine) complex $[(py)_3Cr(CO)_3]$, which was shown to be converted exclusively to $[(py)Cr(CO)_5]$ in the presence of BF_3.

Mechanism of Reaction (1).—Since reaction (1) was followed by observing the disappearance of the complex $[(C_7H_7)M(CO)_3]BF_4$ (M = Cr, Mo, or W), the subsequent fate of the primary product *cis*-$[M(Me(N)_3(CO)_3]$ does not affect the observed kinetics. This was confirmed by the fact that kinetic runs performed under strictly anaerobic conditions using Schlenk tubes yielded rate constants identical to those obtained from runs in which tetra- and penta-carbonyl products were evident. The second-order rate law obtained for reaction (1) over a wide range of nucleophile concentrations (Figure) is consistent with a rate-determining displacement of $C_7H_7^+$ by MeCN, followed by rapid pick-up of another two MeCN ligands.

However, as has been pointed out for the similar reaction of $[(arene)Mo(CO)_3]$ complexes with phosphines,[9] it seems doubtful whether a two-electron donor (*e.g.* MeCN) could replace unaided a seven-electron donor such as $C_7H_7^+$. We therefore favour mechanism (4) in which the bonding of the $C_7H_7^+$ group to the metal alters from involving all seven carbon atoms in the complex $[(C_7H_7)M(CO)_3]BF_4$ to essentially five and finally only three carbon atoms as MeCN ligands (L) are progressively added to the metal. An alternative mechanism, involving a pre-equilibrium (K) association between the complex $[(C_7H_7)M(CO)_3]BF_4$ and MeCN to form a reactive species which then loses $C_7H_7^+$ by unimolecular dissociation (k), can be discounted since



(4)

the rate law for such a mechanism $\{k_{obs} = kK[MeCN]/(1 + K[MeCN])\}$ requires that the reaction will become first order at high [MeCN]. Our reaction with the $[(C_7H_7)Mo(CO)_3]BF_4$ complex is second order to at least 4·5M-MeCN (Figure).

The large negative $\Delta S^\ddagger$ values observed for reaction (1) (Table 2) are also consistent with the proposed displacement mechanism (4). However, they are inconsistent with a pre-equilibrium mechanism, since the negative ΔS^0 of the pre-equilibrium association would be expected to be balanced by the positive entropy contributions of the following dissociation step. The dependence of k_{obs} on the nature of the nitrile nucleophile employed (Table 3) is also expected for an S_N2 process. The higher k_2 value for EtCN as compared to that for MeCN probably arises from the higher inductive effect of the ethyl group, causing EtCN to be a stronger base. It is interesting that the overall order EtCN > MeCN < PhCN is the same as that previously observed [10] for reaction of nitriles with the complex $[Mo(CO)_6]$.

The data in Table 2 show that the ease of displacement of the tropylium cation from the complex $[(C_7H_7)M(CO)_3]BF_4$ decreases markedly in the order Mo > W $\gg$ Cr (850 : 280 : 1). Since the relative rates of displacement are seen to be largely controlled by the $\Delta H^\ddagger$ values (Table 2), the observed order reflects a balance between the ease of M–C_7H_7 bond cleavage and the energy gained by M–NCMe bond formation. The latter is expected to decrease along the series W > Mo > Cr, which therefore indicates the order W > Mo for the strengths of the M–$C_7H_7^+$ bonds in these complexes. It is interesting that both the relative rates of displacement and the $\Delta H^\ddagger$ values observed in the present systems closely parallel those previously observed for reactions of phosphites with arene [11] and cycloheptatriene [12] metal tricarbonyl complexes, suggesting a similarity in mechanism. In a subsequent paper we shall describe the kinetics of the reaction of MeCN on such arene and cycloheptatriene complexes, permitting the first quantitative comparison of the strength of M–C_7H_7 bonds with respect to other π-bonding organic ligands to be made.

[3/103 *Received, 16th January,* 1973]

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[10] K. M. Al-Kathumi and L. A. P. Kane-Maguire, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3759.

[11] A. Pidcock, J. D. Smith, and B. W. Taylor, *J. Chem. Soc.* (*A*), 1967, 872; 1969, 1604.

[12] A. Pidcock and B. W. Taylor, *J. Chem. Soc.* (*A*), 1967, 877.