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KINETICS OF THE REACTIONS OF METHOXIDE ION WITH TRICARBONYL-η-CYCLOHEPTATRIENYL SALTS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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Summary

The kinetics of the reactions of methoxide ion, obtained using triethylamine/*p*-toluenesulphonic acid buffers in methanol, with tricarbonyl-η-cycloheptatrienyl-chromium, -molybdenum and -tungsten tetrafluoroborates have been investigated at 25°C using stopped-flow spectrophotometry. Two separate processes were identified. The first is a fast reversible formation of an initial product which probably arises either by direct attack at the metal or at a carbonyl ligand affording a carbomethoxy complex $[(\eta^7\text{-}C_7H_7)M(CO)_2CO_2Me]$. The second, slower, process involves addition of methoxide ion to the cycloheptatrienyl ring to give the observed product $[(\eta^6\text{-}MeOC_7H_7)M(CO)_3]$. This latter reaction shows metal dependence; the second order rate constants are estimated to be in the proportions 50/10/1 (Cr/Mo/W).

Introduction

A recent communication describing the observation of intermediates when alkoxides attack tricarbonyl-η-cycloheptatrienyl-chromium, -molybdenum and -tungsten salts [1] prompts us to report our findings on the kinetics of some of these reactions. The final product when methoxide ion reacts with the complexes $[(\eta^7\text{-}C_7H_7)M(CO)_3]^+ \ BF_4^-$ (M = Cr, Mo, W) is in all cases the tricarbonyl-7-*exo*-methoxycycloheptatriene derivative [1–3]. Brown, Fitzpatrick and coworkers have shown that shortly after mixing a solution of the molybdenum or tungsten salt with sodium methoxide in methanol at −15°C, the starting complex (I) is rapidly converted into another species (II), and this is followed by the formation of the product (IV).

The production of another species, probably the carbomethoxy complex (III), was also observed in a second dead-end equilibrium. No species corresponding to II or III were detected in the case of the chromium compound.

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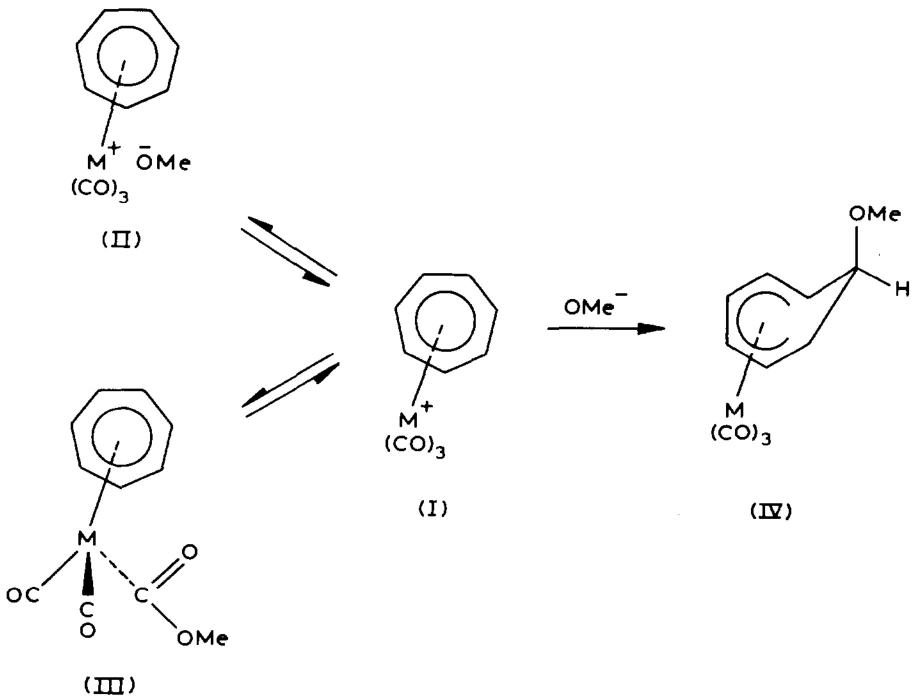

Previous studies have aimed at comparing the stabilities [4] and reactivities [5] of the three metal complexes I (M = Cr, Mo, W). It was found, for example, that the pK_{R^+} values of the cations $[(C_7H_7)M(CO)_3]^+$ in aqueous solution were all very similar [pK_{R^+}, M = Cr 6.3; M = Mo 6.2; M = W ~ 6] [4], although these results have been questioned [6]. Rate constants for the reactions of I with acetylacetone in dichloromethane [5] were in the ratios 5.0/9.5/11.7 (Cr/Mo/W). The rates of addition of tributylphosphine to the ring were also found to be rather insensitive to the metal (2.3/1.0/1.1; Cr/Mo/W) [7]. These results contrast with the large rate differences observed when the nucleophile attacks directly at the metal centre [8]. Significant differences in the rates of nucleophilic addition to the organic ligand are found for corresponding complexes of different metals, however, in the series $[(\eta^5\text{-}C_6H_7)M(CO)_3]^+$ (M = Fe, Ru, Os) [9], $(\eta^6\text{-}C_6H_6)_2M^{2+}$ (M = Fe, Ru, Os) [10] and $[(\eta^6\text{-}C_6H_6)M(CO)_3]^+$ (M = Mn, Re) [11].

The relative rates ($k_{\text{rel.}}$) of methoxide exchange between the salts I and methoxymalachite green in $MeNO_2/MeCOEt$ at 25°C were 1/10/7 (Cr/Mo/W). (cf. $C_7H_7^+$, $k_{\text{rel.}}$ 110) [12]. Rate constants have also been measured for the reaction of methanol with $[C_7H_7Cr(CO)_3]^+$ and for the reverse reaction, protonation of the 7-*exo*-methoxy derivative [6].

Results and discussion

The kinetics of the reaction of methoxide ion with $[(\eta^7\text{-}C_7H_7)M(CO)_3]^+$ BF_4^- (M = Cr, Mo, W) in methanol at 25°C have been measured using visible stopped-flow spectrophotometry. Pseudo-first-order conditions were achieved by using triethylamine/*p*-toluene sulphonic acid buffers which yielded constant concentrations of methoxide ion in the range 1×10^{-6} to 2×10^{-5} mol dm^{-3} [13]. In all three cases a

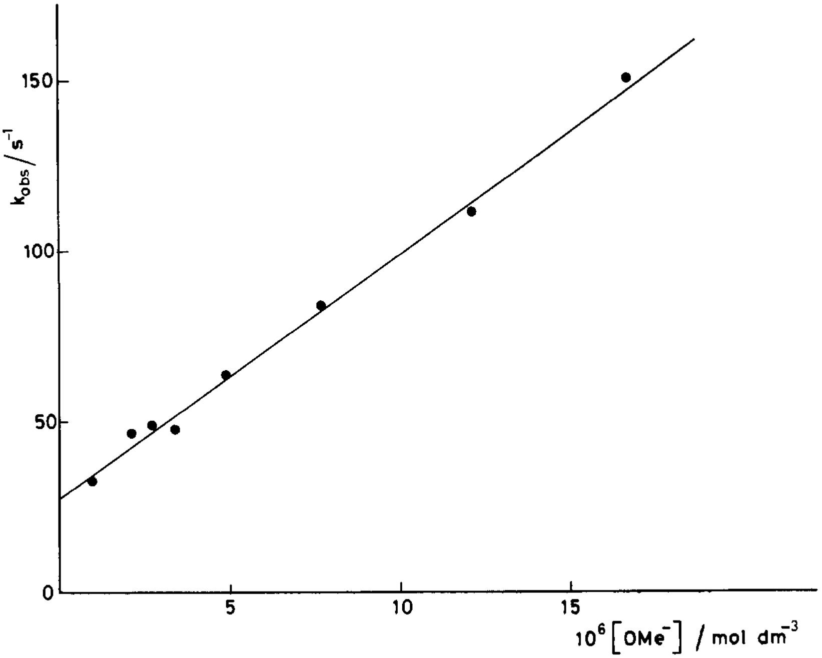

Fig. 1. Variation of observed rate constant with concentration of methoxide for the fast reaction of $[(\eta\text{-}C_7H_7)Mo(CO)_3]^+ BF_4^-$ with methoxide in methanol at 25.0°C.

fast initial reaction was followed by a slower formation of the 7-*exo*-methoxycycloheptatriene product. With M = Cr, the fast initial step merged into the second slower step, so that rate constants for the former could not be evaluated.

The dependence of the observed rate constants on the concentration of methoxide ion for the fast and the slow reactions of the molybdenum complex are shown in Figs. 1 and 2, respectively. For the former k_{obs} was found to be proportional to the methoxide ion concentration, indicating overall second order kinetics for the forward reaction. The observation of a positive intercept on the k_{obs} axis can be interpreted in terms of the reverse reaction, the dissociation of the adduct, which could have structure II or III. In this case $k_{obs} = k_1[A] + k_{-1}$.

The slow reaction showed pseudo-first-order kinetics with respect to the starting complex. On account of the interfering fast reaction, the initial slope of the plot of the logarithm of absorbance against time was greater than expected for a simple reaction for M = Cr, and to some extent also for M = Mo, so that this initial period had to be discarded when evaluating the rate constants. At high methoxide ion concentrations a limiting rate was reached such that k_{obs}(lim) fell in the order Cr > Mo > W in the ratio 28/5/1. As the methoxide ion concentration was reduced, the value of k_{obs} fell, tending to overall second order kinetics. This fall off in k_{obs} was observed only for M = Cr and Mo. A possible explanation of these results is as follows:

$$\underset{(B)}{\text{II or III}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(A)}{[(\eta^7\text{-}C_7H_7)M(CO)_3]^+} + OMe^- \xrightarrow{k_2} \underset{(C)}{[(7\text{-}MeOC_7H_7)M(CO)_3]}$$

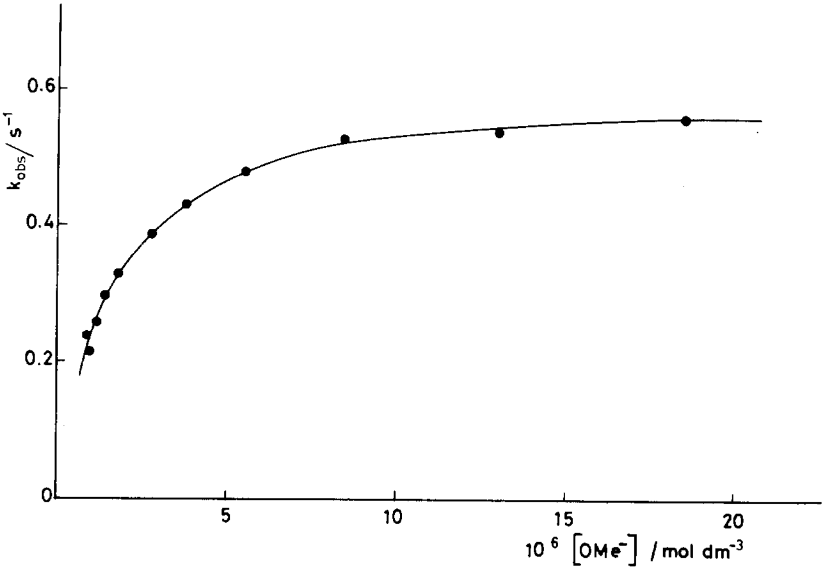

Fig. 2. Variation of observed rate constant with concentration of methoxide for the slow reaction of $[(\eta\text{-}C_7H_7)Mo(CO)_3]^+ BF_4^-$ with methoxide in methanol at 25.0°C.

If k_1 and k_{-1} are large compared with k_2, which is true for M = Mo and W but is only an approximation for M = Cr, we can write

$$K = k_1/k_{-1} = \frac{[B]}{[A][\mathrm{OMe}^-]}$$

$$[A]_{\mathrm{obs}} = [A] + [B] \text{ where } [A]_{\mathrm{obs}} = \text{the observed concentration of } A$$

$$= [A](1 + K[\mathrm{OMe}^-])$$

$$\mathrm{Rate} = k_{\mathrm{obs}}[A]_{\mathrm{obs}} = k_{\mathrm{obs}}[A](1 + K[\mathrm{OMe}^-]) = k_2[A^-][\mathrm{OMe}^-]$$

$$\therefore k_{\mathrm{obs}} = \frac{k_2[\mathrm{OMe}^-]}{1 + K[\mathrm{OMe}^-]}$$

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_2[\mathrm{OMe}^-]} + \frac{K}{k_2}$$

Therefore a plot of $1/k_{\mathrm{obs}}$ against $1/[\mathrm{OMe}^-]$ gives a straight line, from which k_2 and K can be evaluated. The reciprocal plot for the molybdenum system is shown in Fig. 3. A similar plot was obtained for the chromium reaction.

The values of k_{obs}(limiting), k_1 and k_{-1} (obtained from measurements on the fast reaction), k_2 and K (obtained from measurements on the slow reaction) are given in Table 1.

These results (assuming that the interpretation is correct) show that for the direct attack of methoxide ion on the cycloheptatrienyl ring there is a significant metal dependence (Cr > Mo > W). This agrees with the suggestion that this ring is more electrophilic in the chromium than in the molybdenum complex [14]. The approximate values of the equilibrium constant K for the initial association of methoxide

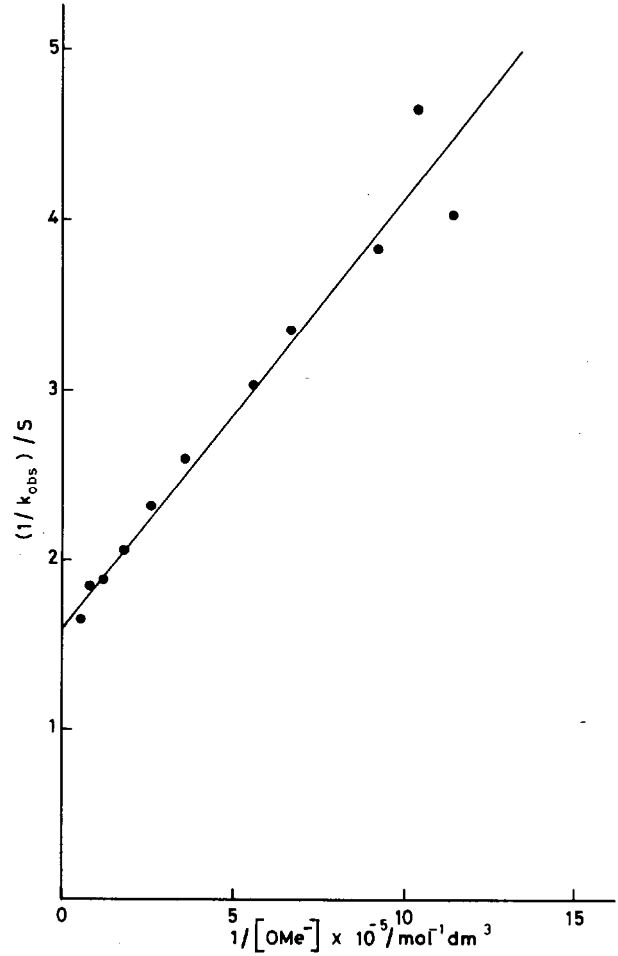

Fig. 3. Reciprocal kinetic plot for the slow reaction $[(\eta\text{-}C_7H_7)Mo(CO)_3]^+ BF_4^- + OMe^-$ in methanol at 25.0°C.

ion with the cation in the 'dead-end' step indicate that this association is equally favoured for all three metals, in agreement with the prediction of molecular orbital calculations [15]. Presumably the side 'intermediate' was not observed spectroscopi-

TABLE 1

KINETIC DATA FOR THE REACTIONS OF $[(\eta^7\text{-}C_7H_7)M(CO)_3]^+ BF_4^-$ WITH METHOXIDE ION IN METHANOL AT 25.0±0.1°C

	M = Cr	M = Mo	M = W
k_{obs}(limiting) (s^{-1})	3.4	0.61	0.12
k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	2.1×10^6	4.1×10^5	4.2×10^4
k_1 ($dm^3\ mol^{-1}\ s^{-1}$)	–	7.3×10^6	3.5×10^6
k_{-1} (s^{-1})	–	28	10
K^a ($mol\ dm^{-3}$)	$5\ \times10^5$	$6\ \times10^5$	–
K^b ($mol\ dm^{-3}$)	–	$3\ \times10^5$	$4\ \times10^5$

[a] From reciprocal plot. [b] $K = k_1/k_{-1}$.

cally in the chromium system [1] because its rate of formation is comparable with that of direct attack of methoxide ion on the ring in this case.

The rate constant for the reaction of methanol with $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+ BF_4^-$ is $0.07\ s^{-1}$ at 25°C [6]. A correction for this has been applied to the k_{obs} values in making the reciprocal plot. No comparable correction has been made to the results for the molybdenum and tungsten complexes.

Experimental

The complexes $[(C_7H_7)Cr(CO)_3]^+ BF_4^-$ [16], $[(C_7H_7)Mo(CO)_3]^+ BF_4^-$ [17] and $[(C_7H_7)W(CO)_3]^+ BF_4^-$ [18] were prepared by previously described methods.

p-Toluenesulphonic acid monohydrate was dehydrated and recrystallised from acetone and then dried in vacuo. Triethylamine was distilled under dry nitrogen from calcium hydride and methanol from magnesium methoxide. Buffer solutions were prepared assuming $pK_b(Et_3N)$ [19] = 10.88 and $pK_{ap}(MeOH) = 16.94$ [20].

Kinetics were followed using a Nortech Canterbury SF3A Mk.III stopped flow spectrophotometer at 390 nm. The output from the photomultiplier was passed to a Datalab DL901 transient recorder and rate constants calculated using a Commodore PET Minicomputer [21]. About ten reactions were carried out at each concentration of methoxide. The concentration of complex was 5×10^{-4} mol dm^{-3} after mixing in the spectrophotometer cell.

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