Kinetics and Mechanism of the Oxygen-transfer Reaction between Bis(diethyldithiocarbamato)dioxomolybdenum(VI) and Triphenylphosphine

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The kinetics of the oxygen-transfer reaction from $[MoO_2(S_2CNEt_2)_2]$ to PPh_3 in acetonitrile solution have been monitored using stopped-flow techniques at temperatures between 15 and 45 °C. The rate law $d[Mo^{IV}]/dt = k_2[Mo^{VI}][PPh_3]$, with $k_2(25\ °C) = 1.1 \pm 0.3\ dm^3\ mol^{-1}\ s^{-1}$, describes the kinetic data obtained, with activation parameters at 25 °C of $\Delta H^{\ddagger} = 8.4 \pm 0.5\ kcal\ mol^{-1}$ and $\Delta S^{\ddagger} = -30 \pm 1.6\ cal\ K^{-1}\ mol^{-1}$.

BARRAL *et al.*[1] reported that the complexes $[MoO_2(S_2CNR^1{}_2)_2]$ ($R^1 = Et$, Pr^n, or Bu^i) oxidise the tertiary phosphines $PR^2{}_3$ ($R^2 = Bu$ or Ph) in chlorobenzene solutions according to (1) and (2). For $R^1 = Pr^n$, the

$$[MoO_2(S_2CNR^1{}_2)_2] + PR^2{}_3 \longrightarrow [MoO(S_2CNR^1{}_2)_2] + PR^2{}_3O \quad (1)$$

$$[MoO(S_2CNR^1{}_2)_2] + [MoO_2(S_2CNR^1{}_2)] \overset{K}{\rightleftharpoons} [Mo_2O_3(S_2CNR^1{}_2)_4] \quad (2)$$

value of K at 41 °C was determined as $4 \times 10^{-3}\ dm^3\ mol^{-1}$ The introduction of dioxygen into this system converts $[MoO(S_2CNR^1{}_2)_2]$ into $[MoO_2(S_2CNR^1{}_2)_2]$ and therefore this type of molybdenum centre is capable of catalysing the conversion of a tertiary phosphine into the corresponding phosphine oxide by dioxygen, and Barral *et al.* reported kinetic data for this catalysis. McDonald and Shulman [2] subsequently reported that the reduction of a large excess of $[MoO_2(S_2CNEt_2)_2]$ by PPh_3 in benzene solution provided a sensitive and accurate method for the determination of small quantities of PPh_3 by spectrophotometric assessment of the amount of $[Mo_2O_3(S_2CNEt_2)_4]$ formed as a result of (2). These latter workers also reported kinetic data for the production of $[Mo_2O_3(S_2CNEt_2)_4]$ under these conditions.

EXPERIMENTAL

The complex $[MoO_2(S_2CNEt_2)_2]$ was prepared as described by Moore and Larson [3] and the orange powder thus obtained was recrystallised from dry benzene to yield the analytically pure complex as a bright yellow microcrystalline material. Triphenylphosphine and PPh_3O (B.D.H) were used as supplied. Sodium diethyldithiocarbamate was dried by repeated azeotropic distillation from benzene and stored under purified dinitrogen until required. Acetonitrile was purified and dried by double distillation from CaH_2 under an atmosphere of purified dinitrogen immediately before use and stored in a serum-capped amber bottle after further degassing with purified dinitrogen. Conductivity studies indicated that $[MoO_2(S_2CNEt_2)_2]$ dissolved in dry MeCN as a non-electrolyte. Solutions of $[MoO_2(S_2CNEt_2)_2]$ in MeCN deteriorated on standing for several hours; therefore aliquot portions (10 cm³) of this solution were prepared immediately prior to use. Furthermore, this deterioration was more pronounced for concentrated solutions and therefore dilute ($<10^{-3}$ mol dm⁻³) $[MoO_2(S_2CNEt_2)_2]$ solutions were used. The course of reaction (1) was sensitive to the presence of trace amounts of water and/or dioxygen; therefore the solutions were transferred using syringe techniques under a positive pressure of purified dinitrogen.

The absorption spectrum of $[MoO(S_2CNEt_2)_2]$ in MeCN solution at various concentrations was recorded on a Perkin-Elmer 402 spectrophotometer and shown to obey Beer's law over the concentration range used in this study. The i.r. and u.v. visible spectral properties of the molybdenum-containing product of the reaction were identical to those obtained for $[MoO(S_2CNEt_2)_2]$ prepared as described by Jowitt and Mitchell.[4]

Kinetic Measurements.—Solutions of the reactants in MeCN were transferred to the storage chambers of an Aminco–Morrow stopped-flow apparatus coupled to a Beckman spectrophotometer. A purified dinitrogen atmosphere was maintained above the solutions, which were thermostatted for 15—20 min prior to reaction to within ±0.1 °C of temperatures between 15 and 45 °C. The temperature of the thermostatting water was recorded before and after circulation and these temperatures generally agreed to within ±0.1 °C. Kinetic measurements at >45 °C were precluded by the volatility of the solvent, and at <15 °C the viscosity of the phosphine solution produced considerable refraction effects on mixing with the molybdenum solution making the absorbance measurements unreliable.

Pseudo-first-order conditions were used to study reaction (1), a greater than 10-fold excess of PPh_3 being maintained over $[MoO_2(S_2CNEt_2)_2]$. A single-stage rate process for the production of $[MoO(S_2CNEt_2)_2]$ was observed under all the conditions employed. A very slow reaction involving the disappearance of $[MoO(S_2CNEt_2)_2]$ was also observed; however, reliable data could not be obtained for this process. Reaction (1) was followed by monitoring transmittance changes at 514 nm, the data being collected and stored on an Aminco-Morrow Dasar system, and subsequently analysed

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[1] R. Barral, C. Bocard, I. Serée de Roch, and L. Sajus, *Tetrahedron Letters*, 1972, 1693.

[2] D. B. McDonald and J. I. Shulman, *Analyt. Chem.*, 1975, **47**, 2023.

[3] F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1976, **6**, 998.

[4] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1969, 2632.

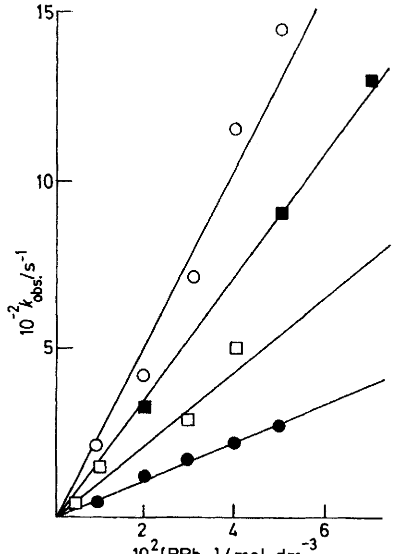
using the program DASAR 2 of Dr. J. P. Day. Rate constants for this reaction were determined from computer plots of log ($D_\infty - D_t$) against time (D_∞ = optical density after 10 half-lives, D_t = optical density at time t). Activation parameters were computed using a least-squares analysis * with equal weighting for all the points.

Kinetic data were also obtained for reaction (1) in the presence of added PPh_3O and $Na[S_2CNEt_2]$.

Kinetic data for the oxygen-transfer reaction between $[MoO_2(S_2CNEt_2)_2]$ and PPh_3

θ_c/°C	$10^4[MoO_2(S_2CNEt_2)_2]$ / mol dm^{-3}	$10^2[PPh_3]$ / mol dm^{-3}	$10^2k_{obs.}$ * / s^{-1}
15.0	5.0	1.0	0.57
	5.0	2.0	1.21
	5.0	3.0	1.72
	5.0	4.0	2.24
	5.0	5.0	2.74
25.0	5.0	0.5	0.42
	5.0	1.0	1.72
	5.0	3.0	2.96
	5.0	4.0	5.20
35.0	5.0	2.0	3.30
	5.0	5.0	9.08
	5.0	7.0	12.50
45.0	5.0	1.0	2.09
	5.0	2.0	4.22
	5.0	3.0	7.27
	5.0	4.0	11.71
	5.0	5.0	14.66

* Typically an average of two measurements.



Observed variation of k_{obs} with $[PPh_3]$ at 15 (●), 25 (□), 35 (■), and 45 °C (○)

RESULTS AND DISCUSSION

Plots of log ($D_\infty - D_t$) against time were generally linear to at least 85% completion of reaction and the values of $k_{obs.}$ obtained at 15, 25, 35, and 45 °C at the concentrations of $[MoO_2(S_2CNEt_2)_2]$ and PPh_3 used in this study are listed in the Table. The dependence of $k_{obs.}$ on $[PPh_3]$ is shown in the Figure. Hence the rate law (3) is applicable with the values of k_2 at 15, 25, 35, and 45 °C being calculated at 0.6, 1.1, 1.8, and 2.8 (±0.2) dm^3 mol^{-1} s^{-1}, respectively. The value for k_2 of 2.3 dm^3 mol^{-1} s^{-1} reported by Barral *et al.* for the rate of oxidation of PPh_3 by $[MoO_2(S_2CNPr^n{}_2)_2]$ in *o*-dichlorobenzene at 41 °C thus agrees well with these data. At 25 °C, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were estimated to be 8.4 ± 0.5 kcal mol^{-1} and -30 ± 1.6 cal K^{-1} mol^{-1}.† Under conditions where the concentrations of $[MoO_2(S_2CNEt_2)_2]$ and PPh_3 were maintained at constant values and PPh_3O or $Na[S_2CNEt_2]$ was included in the reactant medium, no significant effects on the rate constants were observed. Therefore, we interpret the kinetic information obtained in this study in terms of a simple bimolecular mechanism involving an interaction between one $[MoO_2(S_2CNEt_2)_2]$ and one PPh_3 molecule in the activated complex. This interaction could lead to transfer of an oxygen atom *via* the donation of the lone pair of electrons of the phosphorus atom into the Mo–O π^* d_{xy} orbital, thus leading to the formation of the P–O bond and an oxomolybdenum(IV) complex. Such a mechanism could explain the rather low value obtained for $\Delta H^\ddagger$ since the formation of the activated complex requires no significant bond breaking nor any appreciable intramolecular reorganisation(s).

$$d[MoO(S_2CNEt_2)_2]/dt = k_2[MoO_2(S_2CNEt_2)_2][PPh_3] \quad (3)$$

The interpretation of the experimental data assumes that all the absorption observed at 514 nm was due to $[MoO(S_2CNEt_2)_2]$, although $[Mo_2O_3(S_2CNEt_2)_4]$ also absorbs quite strongly at this wavelength.[5] Under the experimental conditions employed, no $[Mo_2O_3(S_2CNEt_2)_4]$ was detected in the reaction products and the kinetic data obtained here, when compared to the results of McDonald and Shulman,[2] indicate that no interference from $[Mo_2O_3(S_2CNEt_2)_4]$ formation should occur. Thus, McDonald and Shulman reported that in benzene solution, the second-order rate constant for $[Mo_2O_3(S_2CNEt_2)_4]$ production is 0.12 dm^3 mol^{-1} s^{-1}. Hence in the reaction sequence (1) ⟶ (2), the rate-determining step appears to be the combination of the molybdenum-(VI) and -(IV) complexes to produce the dimeric molybdenum(V) species. Under the conditions of this study, with a greater than 10-fold excess of PPh_3, $[MoO_2(S_2CNEt_2)_2]$ will effectively be completely converted into $[MoO(S_2CNEt_2)_2]$ before any reaction between these molybdenum-(VI) and -(IV) complexes occurs. For the relative concentrations of the reactants listed in the Table, the rate of $[MoO(S_2CNEt_2)_2]$ production appears to be two to three orders of magnitude greater than the rate of $[Mo_2O_3(S_2CNEt_2)_2]$ formation.

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* This analysis was carried out using the computer program ARRHENIUS I of Dr. J. P. Day.

† Throughout this paper: 1 cal = 4.184 J.

[5] W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, 1974, **13**, 1100.