Pergamon

PII: S0277-5387(96)00568-2

Polyhedron Vol. 16, No. 13, pp. 2163–2167, 1997

0277–5387/97 $17.00+0.00

Kinetic studies of the oxygen-atom transfer reactions between bis(diethyldithiocarbamato)dioxomolybdenum and triphenylphosphine

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(Received 27 September 1996; accepted 15 November 1996)

Abstract—The kinetics of the oxygen-atom transfer reactions from bis(diethyldithiocarbamato)dioxomolybdenum [$MoO_2(S_2CNEt_2)_2$] to triphenylphosphine (PPh_3) in several nonaqueous organic solvents were studied in detail by means of the stopped-flow technique at temperatures between 25 and 40°C. The kinetic and activation parameter data for the oxygen-atom transfer reactions in several nonaqueous solutions were obtained. It was found that the rate constants and the activation energies follow linear relationships *vs* the function of the refractive index $(n^2-1)/(2n^2+1)$. In addition, it was also observed that the pre-exponential factor increases slightly with a decrease of $(n^2-1)/(2n^2+1)$. Furthermore, two linear equations between the rate constant and the activation energy *vs* $(n^2-1)/(2n^2+1)$ with good correlation coefficients were obtained. A one-step mechanism which supposes that the electrons of the lone pair on the P atom of triphenylphosphine enters directly into the π^* antibonding orbital, which makes the Mo=O bond break, was proposed.

Keywords: bis(diethyldithiocarbamato)dioxomolybdenum; triphenylphosphine; oxygen-atom transfer reaction; stopped-flow technique; kinetics; reaction mechanism.

Much attention has been paid recently to the investigations of the behavior of molybdenum in some enzymes. It is well known that some of the molybdoenzymes catalyse net oxygen-atom transfer (OAT) reactions [1–3]. Many results bear evidence of molybdenum existing in the form of the MoO_2^{2+} group in several important enzymes. Therefore, more investigations on compounds containing such a group have been carried out. In examining the reactions carried out by xanthine, sulfite and aldehyde oxidase, and also nitrate reductase, it was found that the only difference between the substrate before and after the reaction is the addition or removal of an oxygen atom. The two-electron oxygen-atom transfer reaction may be relevant to the understanding of the reactions of molybdoenzymes [4]. $MoO_2(S_2CNEt_2)_2$ is one of the important model compounds possessing the MoO_2^{2+} group [5]. It is because of these characteristics of $MoO_2(S_2CNEt_2)_2$ that have been discovered in some molybdenum enzymes [6] that much more efforts have been made to study the model compounds of molybdenum and their oxidizing and reducing reactions [3].

The kinetics for the reaction of $MoO_2(S_2CNEt_2)_2$ with triphenylphosphine (PPh_3) have been studied in a limited way in these organic solvents, namely C_6H_6, MeCN and 1,2-$C_2H_4Cl_2$ [7–9]. However, it is impossible to obtain systematic rules from the literature because different methods for the kinetic investigations and data processing were used and, moreover, as yet, these studies did not extend beyond establishing a bimolecular rate law based on the first-order dependence both on the concentration of $MoO_2(S_2CNEt_2)_2$ and that of PPh_3 and the effect of the solvents used was not investigated. At the same time, the intimate mechanisms of the molybdenum

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enzymes have yet to be fully elucidated. Therefore, much further work, including chemical modeling, needs to be carried out in this field.

Here we report our detailed studies of the chemical kinetics of the reactions of $MoO_2(S_2CNEt_2)_2$ with PPh_3 in the following nonaqueous organic solvents: C_6H_5Br, C_6H_5Cl, *m*-$C_6H_4(CH_3)_2$, C_6H_6, $C_6H_5OCH_3$, $C_6H_5CH_3$, $CHCl_3$, 1,2-$C_2H_4Cl_2$, CH_2Cl_2 and CCl_4. The kinetic parameters, for example, the activation energies and the pre-exponential factors have been obtained. The relationships between the kinetic parameters and the properties of the solvents as well as the reaction mechanism for the OAT reaction are studied and discussed.

EXPERIMENTAL

Materials

Bis(diethyldithiocarbamato)dioxomolybdenum [i.e. $MoO_2(S_2CNEt_2)_2$, denoted as MoO_2L_2 hereinafter, where L = S_2CNEt_4] was synthesized according to the method reported in the literature [10] and was recrystallized from dry benzene–hexane. Triphenylphosphine (PPh_3) was twice recrystallized from ethanol–water. Solvents were AR grade or above. All the solvents employed were dried by 4A molecular sieves which had been pre-treated appropriately and were distilled before use.

Kinetic measurements

Current evidence supports the transfer of an oxygen atom between $Mo^{IV/VI}$ and substrate [11]. Nucleophilic attack by PPh_3 on $MoO_2(S_2CNEt_2)_2$ leads to oxygen-atom transfer, two-electron reduction of molybdenum and oxidation of phosphorus. It is believed that the reaction between $MoO_2(S_2CNEt_2)_2$ and PPh_3 includes two steps [9]:

$$\text{(i)}\ MoO_2(S_2CNEt_2)_2 + PPh_3 \xrightarrow{k_1} MoO(S_2CNEt_2)_2 + OPPh_3$$

$$\text{(ii)}\ MoO_2(S_2CNEt_2)_2 + MoO(S_2CNEt_2)_2 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Mo_2O_3(S_2CNEt_2)_4$$

The reactions are sensitive to the presence of trace amounts of water and/or oxygen, therefore, the solutions were transferred using the syringe technique under a positive pressure of purified and dried nitrogen. Kinetic measurements at temperatures higher than 40°C were precluded by the volatility of several solvents (e.g. the highest reaction temperature for CH_2Cl_2 was 38°C). The kinetics of the initial stage was measured so that we could obtain the kinetic rate constant k_1 of the first step. The reaction for the initial stage is too fast to be determined by the conventional UV spectrometer as described in the literature [10], therefore, the RA-401 stopped-flow spectrophotometer from Union-Giken Co., Japan, was used to monitor the reaction processes.

RESULTS AND DISCUSSION

The determination of the kinetic parameters in various solvents at constant temperature

The changes of the concentration of $MoO_2(S_2CNEt_2)_2$, $[MoO_2L_2]$ with time t were measured spectrophotometrically in various nonaqueous organic solvents at 380 nm. Since the second step of the reaction is biologically irrelevant, it must be prevented in meaningful enzyme models. The experimental results showed that the linear relationship of ln $[MoO_2L_2]$ against t could be obtained at the initial stage, i.e. *ca* 5 s, of the reaction if the concentrations of PPh_3, $[PPh_3]$, were much larger than $[MoO_2L_2]$ [actually, a greater than at least 10-fold excess of PPh_3 was maintained over $MoO_2(S_2CNEt_2)_2$ throughout the kinetic investigations], i.e. pseudo-first-order conditions were used to study the reaction. These phenomena could be explained by second-order kinetics as follows:

$$-d[MoO_2L_2]/dt = k_1[PPh_3][MoO_2L_2]. \quad (1)$$

If $[PPh_3] \gg [MoO_2L_2]$, eq. (1) would become:

$$-d[MoO_2L_2]/dt = k_{obs}[MoO_2L_2], \quad (2)$$

where $k_{obs} = k_1[PPh_3]$. Equation (2) suggests a linear relationship for ln $[MoO_2L_2]$ against time t. From the slope of the straight line, k_{obs} may be obtained. As k_{obs} is proportional to $[PPh_3]$, it is easier to be obtained from the linear relationship of k_{obs} against $[PPh_3]$. The dependence of k_{obs} on $[PPh_3]$ in two solvents 1,2-$C_2H_4Cl_2$ and *m*-$C_6H_5(CH_3)_2$ are exemplified in Fig. 1.

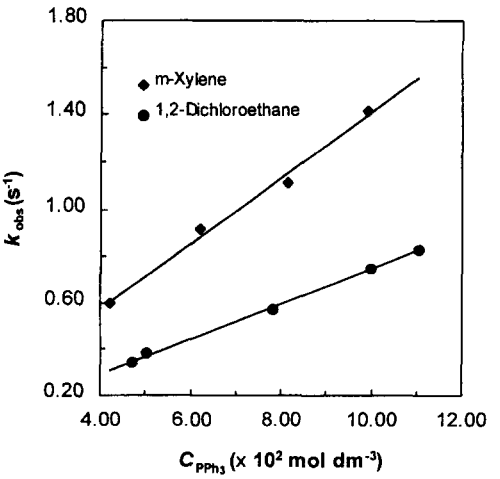


Fig. 1. The observed dependence of k_{obs} on $[PPh_3]$ in *m*-$C_6H_5(CH_3)_2$ and 1,2-$C_2H_4Cl_2$ at 35°C.

Rate constants at different temperatures

The rate constants k_1 determined by the method described above are summarised in Table 1. One can conclude from Table 1 that the rate constants k_1 in the solvents with the phenyl group in their molecules are much larger than those in the solvents of halogenated hydrocarbons.

The relationship between the rate constants and the properties of the solvents

We could not find any definite relationships between the rate constant k_1 and the following properties of the solvents, e.g. dielectric constant ε, $(\varepsilon-1)/(2\varepsilon+1)$, dipole moment, surface tension and viscosity, except for refractive index n. A linear relationship between rate constant and a function of refractive index $(n^2-1)/(2n^2+1)$ could be obtained at different temperatures. The results are shown in Table 2 and Fig. 2. A concrete linear equation between the rate constant k_1 and the function of the refractive index $(n^2-1)/(2n^2+1)$ can be obtained with reasonably good correlation coefficient ($r = 0.967$):

$$k_1(\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}) = 23.6(n^2-1)/(2n^2+1)-4.19. \quad (3)$$

The activation energy and pre-exponential factor as well as their relationships with the properties of the solvents

The activation energies and the pre-exponential factors can be obtained from the Arrhenius plots. The results are summarised in Table 3.

It is noted that the activation energies in the solvents with phenyl group are lower than those in the solvents of the halogenated hydrocarbons. The approximate linear relationship between the activation energy E_a and $(n^2-1)/(2n^2+1)$ can be seen from Fig. 3. This

Table 1. The rate constant k_1 ($\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$) in different solvents at various temperatures

Solvents	25°C	30°C	35°C	40°C
C_6H_5Br	0.59	0.985	1.44	2.20
m-$C_6H_4(CH_3)_2$	0.59	0.92	1.39	2.14
C_6H_5Cl	0.61	0.90	1.37	2.12
C_6H_6	0.49	0.69	1.18	1.82
$C_6H_5OCH_3$	0.48	0.74	1.16	1.59
$C_6H_5CH_3$	0.49	0.74	1.16	1.85
1,2-$C_2H_4Cl_2$	0.24	0.39	0.75	1.04
$CHCl_3$	0.33	0.52	0.73	1.31
CH_2Cl_2	0.24	0.38	0.64	0.93[a]
CCl_4	0.19	0.33	0.52	0.75

[a]Datum obtained at 38°C.

Table 2. The relationship between rate constant k_1 and $(n^2-1)/(2n^2+1)$ in different solvents at 35°C

No.	Solvents	k_1 ($\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$)	n	$(n^2-1)/(2n^2+1)$
1	C_6H_5Br	1.44	1.555	0.243
2	m-$C_6H_4(CH_3)_2$	1.39	1.513	0.231
3	C_6H_5Cl	1.37	1.523	0.234
4	C_6H_6	1.18	1.499	0.227
5	$C_6H_5OCH_3$	1.16	1.496	0.226
6	$C_6H_5CH_3$	1.16	1.492	0.225
7	1,2-$C_2H_4Cl_2$	0.75	1.444	0.210
8	$CHCl_3$	0.73	1.445	0.210
9	CH_2Cl_2	0.64	1.420	0.202
10	CCl_4	0.52	1.457	0.214

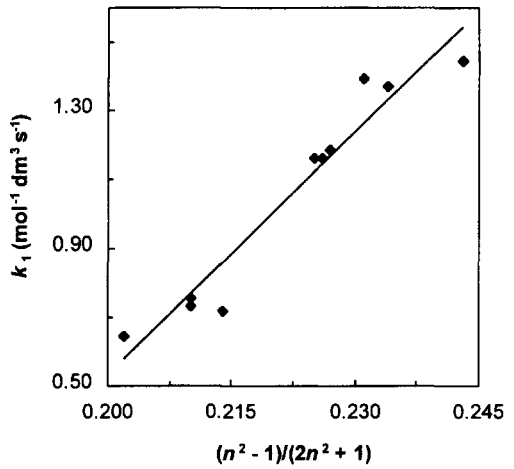


Fig. 2. The variation of the rate constant k_1 with $(n^2-1)/(2n^2+1)$.

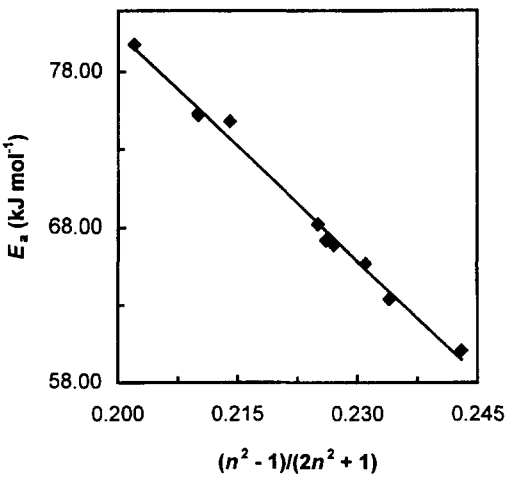


Fig. 3. The dependence of the activation energy E_a on $(n^2-1)/(2n^2+1)$.

variation of the activation energies is contrary to that of the pre-exponential factors.

By analogy with the linear relationship of the rate constant *vs* the function of refractive index $(n^2-1)/(2n^2+1)$, an empirical linear equation between the activation energy and the function of refractive index, $(n^2-1)/(2n^2+1)$, can also be obtained with good correlation coefficient ($r = 0.996$):

$$E_a(\text{kJ mol}^{-1}) = -489.0(n^2-1)/(2n^2+1)+178.3. \quad (4)$$

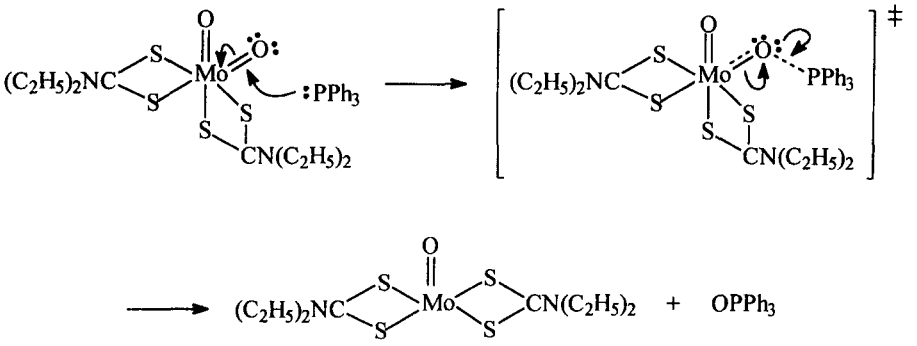
Nevertheless, a deeper understanding of the relationships between the rate constant k_1 and the activation energy E_a against the function of refractive index, $(n^2-1)/(2n^2+1)$, needs further investigation and consideration.

According to the Arrhenius equation, it seems that the increase of the pre-exponential factor would lead to an increase in the values of the rate constants k_1, however, in fact, this was found not to be the case, i.e. the rate constant k_1 decreases with an increase of the pre-exponential factor, but increases with an increase in the function of the refractive index, $(n^2-1)/(2n^2+1)$. This means that the activation energy must exert much more effect on the rate constant than the pre-exponential factor does, i.e. the activation energy would play a main role in the change of the rate constant.

Prior to discussing the reaction mechanism, it is necessary to explain why the pre-exponential factor decreases with an increase of $(n^2-1)/(2n^2+1)$. According to the collision theory of chemical reaction rate, the pre-exponential factor represents the probability of collision between two reactant molecules. If the steric hindrance of the molecule is large, the pre-exponential factor as well as the probability of collision would be lower. It can be seen from Table 3 that the large values of $(n^2-1)/(2n^2+1)$ almost always come from the solvents having the phenyl group. When the molecule of reactant is in the solution, it is surrounded by the molecules of the solvent. The phenyl group has larger molecular radius and could com-

Table 3. The activation energy E_a and pre-exponential factor A in various solvents

No.	Solvents	Activation energy E_a (kJ mol^{-1})	Pre-exponential factor A
1	C_6H_5Br	64.7	1.37×10^{11}
2	m-$C_6H_4(CH_3)_2$	65.2	3.00×10^{11}
3	C_6H_5Cl	65.1	1.44×10^{11}
4	C_6H_6	67.8	3.76×10^{11}
5	$C_6H_5OCH_3$	63.4	8.40×10^{11}
6	$C_6H_5CH_3$	68.0	4.12×10^{11}
7	1,2-$C_2H_4Cl_2$	75.0	6.80×10^{12}
8	$CHCl_3$	69.6	1.02×10^{12}
9	CH_2Cl_2	79.4	1.94×10^{13}
10	CCl_4	73.5	1.44×10^{12}



Scheme 1.

bine with the reactant molecules more tightly so that the reactant would experience much more steric hindrance, therefore, the pre-exponential factor decreases. However, this effect is more than offset by the decrease in activation energy with an increase in the refractive index function $(n^2-1)/(2n^2+1)$.

Reaction mechanism

In the experiments of observing the UV–vis absorption spectra of $MoO_4(S_2CNEt_2)_2$, we found that the maximum absorption wavelength of the π–π^* transition band of Mo=O showed a marked red shift in solvents with the phenyl group. There is a linear relationship between $1/\lambda_{(nm)}$ and $(n^2-1)/(2n^2+1)$. This phenomenon is quite similar to that of the activation energy in this work and lead us to postulate that the π^* antibonding orbital in the Mo=O group will play a very important role for the reaction between $MoO_2(S_2CNEt_2)_2$ and PPh_3. The solvents with the highly polarizable phenyl group would interact on Mo=O much more strongly and reduce the energy of the antibonding orbital of Mo=O bond.

It is obvious that the larger the $(n^2-1)/(2n^2+1)$ of the solvent, the easier the movement of electrons in the molecules of the solvent. Thus the interaction between the solvent molecules and Mo=O would be stronger. Based on these results the reaction mechanism could be proposed as follows: in the course of collision, the interaction between one $MoO_2(S_2CNEt_2)_2$ and one PPh_3 molecule could lead to the transfer of an oxygen atom *via* the donation of the lone pair of the electrons of the phosphorus atom of PPh_3 into the π^* antibonding orbital of the Mo=O bond of $MoO_2(S_2CNEt_2)_2$, thus leading to the formation of the P—O bond and the $MoO(S_2CNEt_2)_2$ complex (Scheme 1).

It has been pointed out that, in the process of the reaction between $MoO_2(S_2CNEt_2)_2$ and PPh_3, there is only one step for reducing Mo^{VI} to Mo^{IV} and without the intermediate stage of the biologically unimportant Mo^V species. ESR experiments failed to reveal the existence of the Mo^V intermediate. Under the conditions of the present work, with a greater than at least 10-fold excess of PPh_3, $MoO_2(S_2CNEt_2)_2$ will be fully converted into $MoO(S_2CNEt_2)_2$ before any reaction between $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$ occurs. If we accept the mechanism suggested above, the one step process is explained clearly.

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