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# Kinetics and mechanism of deoxygenation of (*N*-salicylidene-2-aminophenolato)-(ethanol)dioxomolybdenum(VI) by thionyl chloride

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**Abstract**—The kinetics of deoxygenation of [$MoO_2$(Sap)EtOH] ($Sap^{2-}$ = *N*-salicylidene-2-aminophenolate dianion) by thionyl chloride have been studied in acetonitrile and a mixture of tetrahydrofuran and acetonitrile (v/v = 9 : 1) by spectrophotometry. Under the conditions [$MoO_2$(Sap)EtOH] ≪ [$SOCl_2$], the reaction of formation of the product MoO(Sap)$Cl_2$ consists of two consecutive steps. The pseudo-first-order rate constants of the first-step reaction depended on $[SOCl_2]^{1/2}$ and were significantly affected by the dielectric constant of solvent used, whereas those of the second-step reaction were independent of [$SOCl_2$]. A mechanism is proposed for the deoxygenation, where the reactant reacted initially with $MoO_2$(Sap)EtOH is not $SOCl_2$, but $SOCl^+$ or $Cl^-$ ions. © 1997 Elsevier Science Ltd

*Keywords*: dioxomolybdenum(VI); thionyl chloride; deoxygenation; kinetics; intermediate; self-ionization.

Much of the coordination chemistry of $Mo^{VI}$ is centered on classes of complexes containing the *cis*-dioxo $MoO_2^{2+}$ cation, but species containing the oxo ligand $MoO^{4+}$ are rarely found. Examples of cases where the unit is found include seven-coordinate peroxo and persulfido complexes, $MoO(X_2)L_4^{2+}$ (X = O, S), seven-coordinate dithiocarbamate complexes, $MoO(dtc)_3^+$, and five-coordinate oxyhalides, $MoOX_4$ [1]. To our knowledge, the only example of a mononuclear $MoO^{4+}$ center with a coordination number of six is MoO(cat)(Sap)(cat = catecholate dianion) [2], where the terminal oxo ligand and the central nitrogen donor of the Sap ligand occupy opposite vertices of the octahedron.

In this study the kinetics of reaction of $MoO_2$(Sap)EtOH with $SOCl_2$ have been studied in acetonitrile and a mixture of tetrahydrofuran (THF) and acetonitrile (v/v = 9 : 1). The product of the reaction is a six-coordinate oxomolybdeum(VI) complex, as expressed by the equation.

$$MoO_2(Sap)EtOH + SOCl_2 \longrightarrow MoO(Sap)Cl_2 + SO_2 + EtOH \quad (1)$$

The deoxygenation of oxovanadium(IV) complexes with polydentate ligands by $SOCl_2$ readily yielded *trans*-dichlorovanadium(IV) complexes [3–5]. Floriani and co-workers assumed that an acid–base adduct between the complexes and $SOCl_2$ was formed as an intermediate [3]. Salem and Amer studied the kinetics of the deoxygenation in *N*,*N*-dimethylformamide and reported that the reaction obeys second-order kinetics [6].

## EXPERIMENTAL

### *Materials*

The complex [$MoO_2$(Sap)EtOH] was synthesized from $MoO_2$(acetylacetonate)$_2$ according to the method described in the literature [7]. Solvents were purified by distillation under dry dinitrogen before use: THF(Kanto Chemical Co.), *n*-hexane (Kanto)

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and diethyl ether (Kanto) from sodium/benzophenone; acetonitrile from calcium hydride. Thionyl choride (Kanto) was distilled before use.

The complex $MoO(Sap)Cl_2$ was prepared as follows: A 3.85 g (0.01 mol) sample of $MoO_2(Sap)EtOH$ was dissolved in 100 $cm^3$ THF and the solution was filtered. To the filtrate was added 20 $cm^3$ of a THF solution containing 2.16 $cm^3$ (0.03 mol) of thionyl chloride. The color of the reaction mixture turned from orange to deep purple. The purple solution was concentrated to 20 $cm^3$ and then diluted with 30 $cm^3$ hexane. The product was filtered, washed with diethyl ether and dried *in vacuo*. Reactions were carried out under of dry dinitrogen using the standard Schlenk technique. The yield was >85%. Found: C, 39.6; H, 2.3; N, 3.8. Calc. for $C_{13}H_9NO_3Cl_2Mo$: C, 39.6; H, 2.3; N, 3.6%. The IR spectrum of the complex exhibited a strong absorption band at 942 $cm^{-1}$, which is characteristic of the Mo=O stretching in the $MoO^{4+}$ group [1,2].

### *Kinetic measurements*

Pseudo-first-order conditions ([$MoO_2(Sap)EtOH$] [$SOCl_2$]) were used throughout the study of the reaction expressed by eq. (1) and verified by the results that pseudo-first-order rate constants $k_{obs}$ were independent of [$MoO_2(Sap)EtOH$] ($1$–$5 \times 10^{-4}$ M). The constants were determined from the change of absorbance with a lapse of time using Union Giken RA 401 stopped-flow or Shimadzu UV-160A spectrophotometers with thermostated cell compartments.

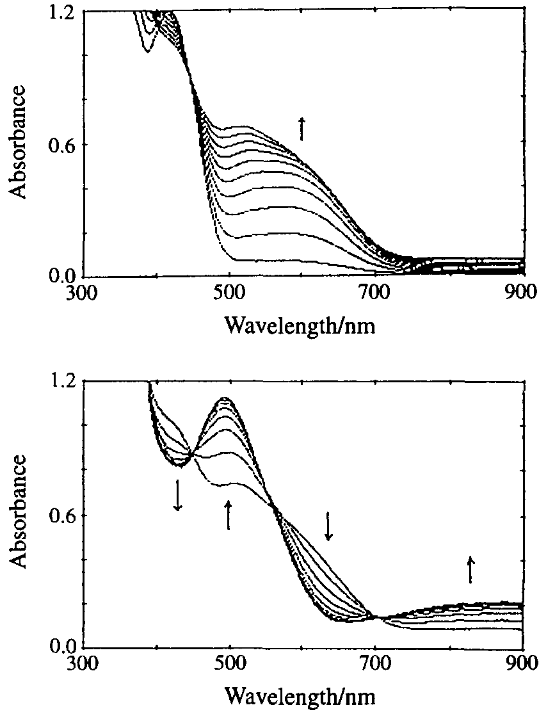

Fig. 1. Spectral changes in the reaction of $1.89 \times 10^{-4}$ M $MoO_2(Sap)EtOH$ with 0.0445 M $SOCl_2$ in a mixture of THF and $CH_3CN$ (v/v = 9 : 1) at 15.4°C. Spectra in the upper figure were recorded at 40 s intervals, whereas spectra in the lower figure were recorded at 600 s intervals after the measurement of spectra in the upper figure.

## RESULTS AND DISCUSSION

Figure 1 shows spectral changes in the reaction of $MoO_2(Sap)EtOH$ with $SOCl_2$ in a mixture of THF and $CH_3CN$ (v/v = 9 : 1). As the reaction proceeded, the absorbance of the broad band at *ca* 600 nm increased at high rate and then decreased at low rate. The UV–vis electronic absorption spectrum measured at the end point of the reaction was the same as that of $MoO(Sap)Cl_2$. Therefore, the reaction (1) is considered to consist of two consecutive steps, whose pseudo-first-order rate constants are $k_{1,obs}$ and $k_{2,obs}$:

$$MoO_2(Sap)EtOH\,(A) \longrightarrow \text{Intermediate}\,(B) \longrightarrow MoO(Sap)Cl_2\,(C) \qquad (2)$$

Absorbance measurements were taken at 600 nm as a function of time. A typical trace is illustrated in Fig. 2 where the absorbance rapidly rises and then slowly declines. The traces were analyzed by means of a nonlinear least-squares method, where $k_{1,obs}$, $k_{2,obs}$ and the molar extinction coefficient ($\varepsilon_{int}$) of the intermediate were used as unknown parameters to fit the following equation [8].

$$A_t - A_f = \alpha \exp(-k_{1,obs}t) + \beta \exp(-k_{2,obs}t) \qquad (3)$$

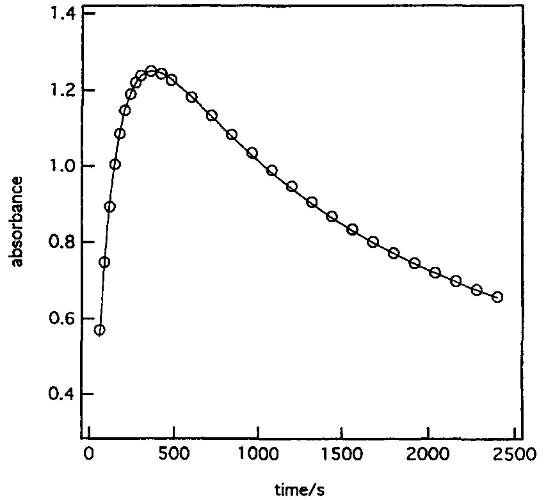

Fig. 2. Change of absorbance at 600 nm as a function of time for the reaction of $1.89 \times 10^{-4}$ M $MoO_2(Sap)EtOH$ with 0.0445 M $SOCl_2$ in a mixture of THF and $CH_3CN$ (v/v = 9 : 1) at 15.4°C. The solid line is that given by nonlinear least-squares fit based on eq. (3).

where $A_t$ and $A_f$ represent the absorbances at times $t$ and infinity, respectively, and $\alpha$ and $\beta$ are:

$$\alpha = [A]_0 \{(\varepsilon_{\text{int}} - \varepsilon_{\text{A}})k_{1,\text{obs}} + (\varepsilon_{\text{A}} - \varepsilon_{\text{C}})k_{2,\text{obs}}\}/ (k_{2,\text{obs}} - k_{1,\text{obs}})$$

$$\beta = [A]_0 (\varepsilon_{\text{C}} - \varepsilon_{\text{int}})k_{1,\text{obs}}/(k_{2,\text{obs}} - k_{1,\text{obs}}), \qquad (4)$$

where $\varepsilon$'s are molar extinction coefficients and $[A]_0$ is the initial concentration of $MoO_2(Sap)EtOH$. As shown in Fig. 2, calculated values agree well with the observed trace giving the best-fit values for $k_{1,\text{obs}}$, $k_{2,\text{obs}}$ and $\varepsilon_{\text{int}}$. Under the condition in Fig. 2, these values were determined to be as follows: $k_{1,\text{obs}} = 8.60 \times 10^{-3}$ $s^{-1}$, $k_{2,\text{obs}} = 6.71 \times 10^{-4}\ s^{-1}$ and $\varepsilon_{\text{int}} = 7.84 \times 10^3\ M^{-1}$ $cm^{-1}$. It is to be noted that the mathematical analysis for such a consecutive reaction as eq. (2) yields an alternative solution with a different set of parameters, $k'_{1,\text{obs}}, k'_{2,\text{obs}}$ and $\varepsilon'_{\text{int}}$, where $k'_{1,\text{obs}} = k_{2,\text{obs}}, k'_{2,\text{obs}} = \text{k}_{1,\text{obs}}, \varepsilon'_{\text{int}} = \varepsilon_{\text{A}} + \text{k}_{1,\text{obs}}(\varepsilon_{\text{int}} - \varepsilon_{\text{A}})/\text{k}_{2,\text{obs}}$ [8]. For example, another set of solution for the condition of Fig. 2 is $k'_{1,\text{obs}} = 6.71 \times 10^{-4}\ s^{-1}$, $k'_{2,\text{obs}} = 8.60 \times 10^{-3}\ s^{-1}$, $\varepsilon'_{\text{int}} = 1.04 \times 10^5\ M^{-1}\ cm^{-1}$. However, the latter set can be ruled out by the following reasoning. The larger rate constants were proportional to $[SOCl_2]^{1/2}$, while the smaller rate constants were independent of $[SOCl_2]$ (see below). The maximum absorbance at 600nm increased with increasing $[SOCl_2]$. These results indicate that the rate constant ($k_{1,\text{obs}}$) of the first step is larger than that ($k_{2,\text{obs}}$) of the second step.

The values of $k_{1,\text{obs}}$ and $k_{2,\text{obs}}$ were determined with changing $[SOCl_2]$ at different temperatures and are plotted against $[SOCl_2]^{1/2}$ and $[SOCl_2]$ in Figs 3 and 4, respectively. As shown in figures, the $k_{1,\text{obs}}$ values vary linearly with $[SOCl_2]^{1/2}$, while the $k_{2,\text{obs}}$ values are independent of $[SOCl_2]$. Nonzero intercepts of $x$ axis in Fig. 3 may be attributed to the loss of $SOCl_2$ by its fast reaction with $H_2O$ ($SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$), the latter being added unintentionally to the reaction mixture.

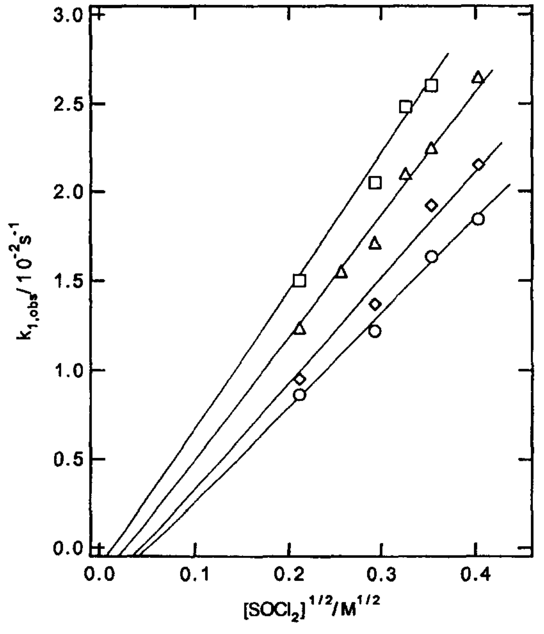

Fig. 3. Plots of $k_{1,\text{obs}}$ *vs* $[SOCl_2]^{1/2}$ for the reaction of $MoO_2$(Sap)EtOH with $SOCl_2$ in a mixture of THF and $CH_3CN$ (v/v = 9 : 1) at various temperatures: ○, 15.4; △, 20.3; ◇, 25.4; □, 30.0°C.

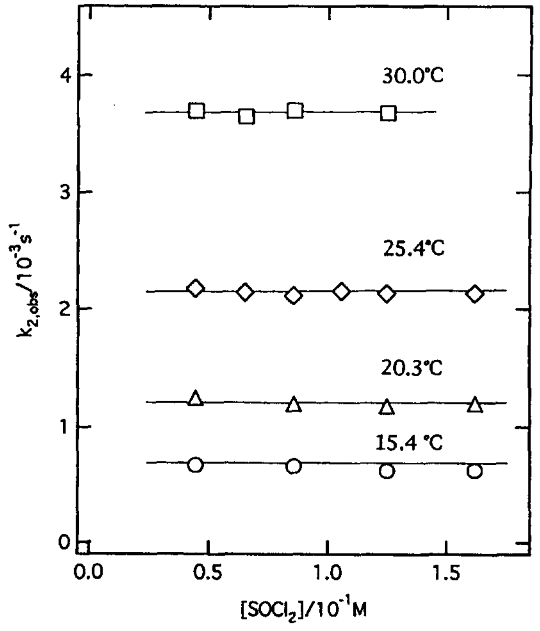

Fig. 4. Plots of $k_{2,\text{obs}}$ *vs* $[SOCl_2]$ for the reaction of $MoO_2$(Sap)EtOH with $SOCl_2$ in a mixture of THF and $CH_3CN$ (v/v = 9 : 1) at various temperatures.

The results obtained in this study might well explained by the mechanism given in Fig. 5. The dependence of $k_{1,\text{obs}}$ on $[SOCl_2]^{1/2}$ indicates that the reactant reacted initially with $MoO_2$(Sap)EtOH is not $SOCl_2$, but $SOCl^+$ or $Cl^-$ ions, i.e. products of self-ionization equilibrium of $SOCl_2$($SOCl_2 = SOCl^+ + Cl^-$) [9]. If the equilibrium constant $K_d$ of the reaction is very small, $[SOCl^+] = [Cl^-] = (K_d[SOCl_2])^{1/2}$. Therefore, the rate of the first-step reaction varies linearly with $[SOCl_2]^{1/2}$.

According to the mechanism, EtOH in $MoO_2$ (Sap) EtOH is rapidly substituted for the $Cl^-$ ion and then the $SOCl^+$ ion attacks a terminal oxo ligand *trans* to $Cl^-$, leading to the formation of an intermediate. If the second-order rate constant of the latter reaction is $k_2$, the slopes in Fig. 3 correspond to $k_2K_d^{1/2}$. The values are listed in Table 1, along with activation parameters.

The fact that the $k_{2,\text{obs}}$ values are independent of $[SOCl_2]$ may be explained by the intramolecular rearrangement where $SO_2$ is evolved. The structure of the final product $MoO(Sap)Cl_2$ is assumed to be the same as that of the corresponding monooxomolybdeum(V) $[MoO(Sap)Cl_2]^-$, where the planar tridentate Schiff base ligand (Sap) occupies meridional positions with N atom *trans* to the terminal

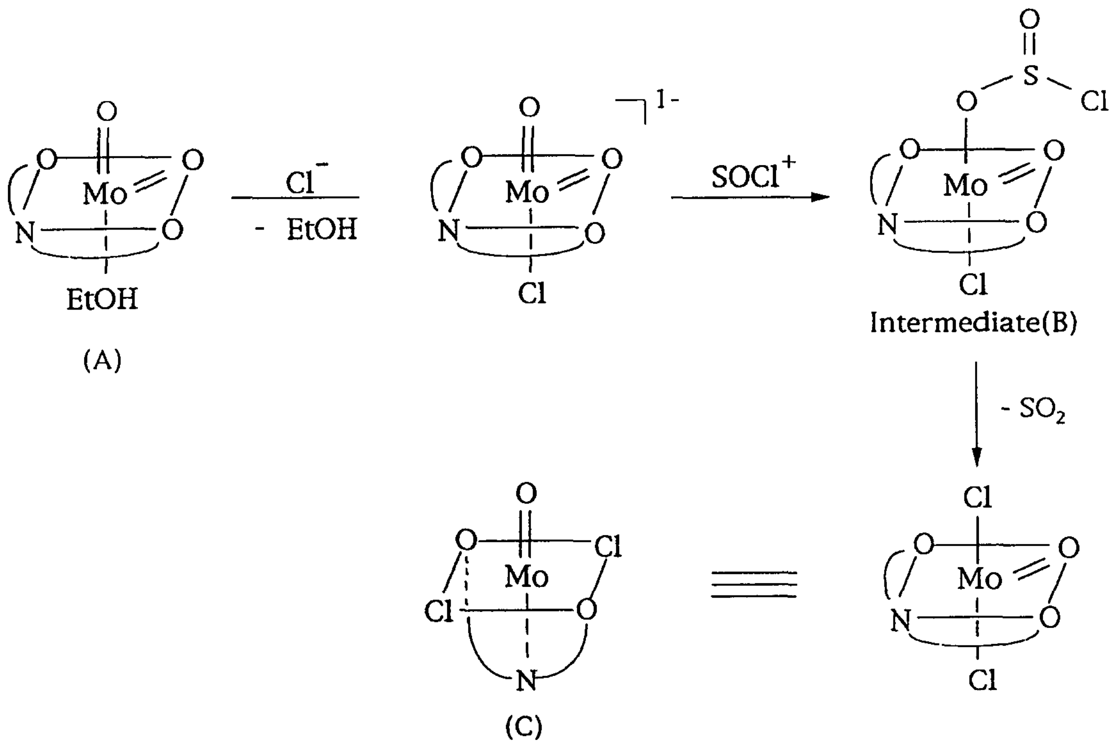

Fig. 5. Possible mechanism for the reaction of $MoO_2(Sap)EtOH$ with $SOCl_2$: ONO represents *N*-salicylidene-2-aminophenolate dianion.

Table 1. Kinetic data for the reaction of $MoO_2(Sap)EtOH$ by $SOCl_2$ in $CH_3CN$ and a mixture of THF and $CH_3CN$ (v/v = 9 : 1)

(a) in a mixture of THF and $CH_3CN$ (v/v = 9 : 1)

| Temperature (°C) | $k_2K_d^{1/2a}$ ($M^{-1}$ $s^{-1}$) | $k_{2,obs}^{b}$ ($s^{-1}$) |
|---|---|---|
| 15.4 | $5.19 \times 10^{-2}$ | $6.44 \times 10^{-4}$ |
| 20.3 | $6.41 \times 10^{-2}$ | $1.21 \times 10^{-3}$ |
| 25.4 | $7.31 \times 10^{-2}$ | $2.15 \times 10^{-3}$ |
| 30.0 | $7.99 \times 10^{-2}$ | $3.66 \times 10^{-3}$ |

$^{a}\Delta H\ddagger = 18.8 \pm 2.5$ kJ $mol^{-1}$, $\Delta S\ddagger = -204 \pm 9$ J $K^{-1}$ $mol^{-1}$.
$^{b}\Delta H\ddagger = 83.6 \pm 0.6$ kJ $mol^{-1}$, $\Delta S\ddagger = -15.8 \pm 1.9$ J $K^{-1}$ $mol^{-1}$.

(b) in $CH_3CN$

| Temperature (°C) | $k_2K_d^{1/2a}$ ($M^{-1}$ $s^{-1}$) | Temperature (°C) | $k_{2,obs}^{b}$ ($s^{-1}$) |
|---|---|---|---|
| 17.2 | 22.9 | 25.0 | $1.19 \times 10^{-3}$ |
| 22.0 | 25.8 | 30.0 | $2.06 \times 10^{-3}$ |
| 27.1 | 27.0 | 35.0 | $3.56 \times 10^{-3}$ |
| 32.0 | 29.4 | 40.0 | $6.09 \times 10^{-3}$ |

$^{a}\Delta H\ddagger = 9.56 \pm 1.56$ kJ $mol^{-1}$, $\Delta S\ddagger = -186 \pm 6$ J $K^{-1}$ $mol^{-1}$.
$^{b}\Delta H\ddagger = 82.0 \pm 0.6$ kJ $mol^{-1}$, $\Delta S\ddagger = -25.9 \pm 1.9$ J $K^{-1}$ $mol^{-1}$.

oxo group and two $Cl^-$ ions are *cis* to the oxo group [10].

The deoxygenation of $MoO_2(Sap)EtOH$ by $SOCl_2$ was also investigated in $CH_3CN$. The rate of the first-step reaction was so fast that the reaction was monitored on the stopped-flow spectrophotometer. The change in absorbance at 600 nm with time was fitted to a single-exponential function and the rate constants $k_{1,obs}$ were obtained. The plots of $k_{1,obs}$ against $[SOCl_2]^{1/2}$ were linear and the slopes ($k_2K_d^{1/2}$) are listed

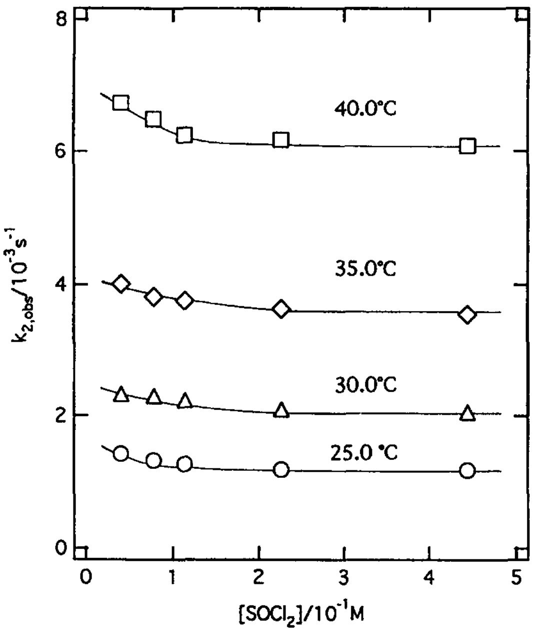

Fig. 6. Plots of $k_{2,obs}$ *vs* $[SOCl_2]$ for the reaction of $MoO_2(Sap)EtOH$ with $SOCl_2$ in $CH_3CN$ at various temperatures.

in Table 1, along with activation parameters. The reason why $k_{1,obs}$ is much larger in $CH_3CN$ than in a mixture of THF and $CH_3CN$ is that the dielectric constant of $CH_3CN$ is larger than that of the mixed solvent. The equilibrium constants $K_d$ of self-ionization of $SOCl_2$ are expected to increase with increasing the dielectric constant of the medium because the neutral molecule of $SOCl_2$ ionizes to oppositely charged ions [11]. The enthalpies of activation for $k_{1,obs}$ in both solvents are small, suggesting that the self-ionization of $SOCl_2$ is exothermic. However, for quantitative evaluation of the enthalpy of activation the dependence of the dielectric constant on temperature must be taken into account: the dielectric constant tends to decrease with increasing temperature [12].

The second-step reaction in $CH_3CN$ was monitored on the UV–vis spectrophotometer and the rate constants $k_{2,obs}$ were obtained from the single-exponential fitting of the change in absobance with time. As shown in Fig. 6, the rate constants decrease very gradually with increasing $[SOCl_2]$ in its low region, but tend to approach limiting values in its high region. The rate constants at the highest $[SOCl_2]$ measured were taken as the limiting values and are listed in Table 1. Considering that the second-step reaction is intramolecular, it seems reasonable that the differences in the $k_{2,obs}$ values and activation parameters are small between both solvents.

The mechanism of Fig. 5 is similar to that proposed for the formation of *gem*-dichlorides from carbonyl compounds by treatment with $SOCl_2$ [13] or $PCl_5$ [14] in that substrates are not initially attacked by $SOCl_2$ or $PCl_5$, but by its separated charged species.

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