Kinetic study of the intermediate in the reaction between picryl chloride and sodium sulphite in aqueous solution

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KINETIC STUDY OF THE INTERMEDIATE IN THE REACTION
BETWEEN PICRYL CHLORIDE AND SODIUM SULPHITE
IN AQUEOUS SOLUTION

By Muneo SASAKI

The reaction between picryl chloride and sulphite ion in aqueous solution takes
place rapidly to give an intense color which is attributed to a 1,3-σ-complex formed by
the reversible attack of a sulphite ion on the C⁻ position of picryl chloride. The color
slowly fades because picryl chloride present at equilibrium is attacked by sulphite ion
to give 1,1-σ-complex which rapidly loses chloride ion to form picryl sulphonate ion
finally. The 1,3-σ-complex dissociates to maintain equilibrium. The rates of appearance
and disappearance of the transient colored species were measured in the range of 15-
35°C by the stopped-flow method. The rate constants at 25°C, activation enthalpies and
activation entropies on each process are shown in Table 2 in the text. The 1,3-σ-complex
was verified by NMR spectrum in DMSO-H₂O solution. The formation of the 1,1-σ-
complex was inferred from the nature of the final products. It may be concluded that
the sulphite attacks on C₁-position and C₃-position take place concurrently and the
former may be accompanied with higher energy barrier.

Introduction

1-X-2, 4, 6-Trinitrobenzene (X=OCH₃, NH₂, NHCH₃, N(CH₃)₂) can react with nucleophiles
such as CH₂O⁻ to form 1,1-σ-complexes (I) and 1,3-σ-complexes (IIa)¹. For several systems studied
well the 1,3-σ-complex is kinetically favored, and formed rapidly although 1,1-σ-complex is more
stable and formed slowly. This is well verified for 2,4,6-trinitroanisole (TNA, X=OCH₃) and CH₂O⁻
in methanol-DMSO, first by Servis by NMR². There are also spectroscopic and kinetic evidences for
the same thing in methanol by Bernasconi³. There are several spectroscopic and kinetic studies on
the reaction of substituted dinitrobenzenes and trinitrobenzenes with CH₂O⁻ in methanol or methanol-
DMSO⁴⁻⁸.

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³) C. F. Bernasconi, J. Amer. Chem. Soc., 93, 6975 (1971)
⁷) F. Terrier, F. Millot and R. Schaal, J. C. S. Perkin II, 1192 (1972)
⁸) M. R. Crampton and H.A. Khan, J. C. S. Perkin II, 733 (1972)
On the other hand, it was found by NY1R that 1-2, 4, 6-trinitrobenzenes react with SO\textsuperscript{2-} to form only stable 1, 3-\(\sigma\)-complex (IIb) in low concentration of SO\textsuperscript{2-} in DMSO-H\textsubscript{2}O\textsuperscript{10}. The reaction of picryl chloride with acetonate ion also gives only 1, 3-\(\sigma\)-complex (III)\textsuperscript{11}. The reactions of 2, 4, 6-trinitrobenzene (TNB) and 1-substituted-TNB with SO\textsuperscript{2-} were kinetically studied in aqueous solution\textsuperscript{12-14}. There are some papers concerned with the reaction of picryl chloride (PicCl) with anionic nucleophiles such as OH\textsuperscript{-} and CH\textsubscript{3}O\textsuperscript{-}.\textsuperscript{8} The interpretation to attribute the transient colored species to 1, 1-\(\sigma\)-complex was criticized\textsuperscript{15-17}, because chloride ion is, in general, a better leaving group than OH\textsuperscript{-} or CH\textsubscript{3}O\textsuperscript{-}.

In this paper the reaction of PicCl with SO\textsuperscript{2-} was studied from the viewpoint of the behavior of the transient species in aqueous solution, in order to clarify the sequence of the substitution reaction.

**Experimentals**

**Materials**

Commercial PicCl was repeatedly recrystallized from ethanol until constant melting point, 83°C. Sodium sulphite and sodium sulphate were crystallized from aqueous solutions by adding ethanol, and dried under reduced pressure at 100°C until constant weight. Conductivity water was used as a solvent. Spectrograde dimethylsulphoxide (DMSO) was used without further purification. The

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13) M. Sasaki, *This Journal*, 43, 44 (1973)
reaction solutions were prepared immediately before the use.

**Apparatus and procedure**

Kinetic measurements were carried out by the use of a Union Giken SF-71 Stopped-Flow Spectrophotometer, which is operated by the gaseous pressure-drive method in which reaction solutions are driven into the mixing chamber by pressurizing the reservoirs with nitrogen gas. The mixing time under this study was about 1.0 msec. Thermostated water was circulated around the observation-cell compartment which contained a 2mm quartz cell, and the reservoirs, and the temperatures were regulated to within±0.1°C.

All kinetic runs were performed with sodium sulphite in large excess over PicCl, whose concentration varied from 25-120 μM. The ionic strength was maintained constant, if necessary, by adding sodium sulphate. The observed first-order rate constants were determined by Guggenheim plots.

The absorption spectra of relatively stable compounds were determined by a Shimadzu UV-200 Spectrophotometer. NMR spectra were recorded with a JEOL-C-60HL (60 MHz) spectrometer.

**Results and Discussions**

**Initial complex formation**

When PicCl, ca. 1mM, was mixed with sodium sulphite in the range 5-100 mM in aqueous solution, a reddish color developed almost instantaneously and faded in about a second. The final visible spectrum of this mixture has a broad maximum near 500 nm and is similar to that of a mixture of sodium picryl sulphonate and sodium sulphite in aqueous solution. This compound is the 1:1 addi...
Table 1  Observed first-order rate constant, $k_{obs}$, for the formation of the initial complex between PicCl (41 μM) and sodium sulphite (3.4 mM) at 25°C.

<table>
<thead>
<tr>
<th>wavelength, nm</th>
<th>$k_{obs}$, sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>80.5</td>
</tr>
<tr>
<td>440</td>
<td>77.5</td>
</tr>
<tr>
<td>460</td>
<td>78.8</td>
</tr>
<tr>
<td>480</td>
<td>76.0</td>
</tr>
<tr>
<td>500</td>
<td>74.0</td>
</tr>
<tr>
<td>520</td>
<td>75.1</td>
</tr>
<tr>
<td>540</td>
<td>79.0</td>
</tr>
</tbody>
</table>

Fig. 2 Stopped-flow spectrum of the initial complex (V) in aqueous solution at 25.0°C. [PicCl]$_b$ = 41 μM, [Na$_2$SO$_3$]$_b$ = 3.42 mM. Optical path length is 2 mm.

Fig. 3  Visible absorption spectra of the initial transient in DMSO-H$_2$O (1:1 v/v) at the following time after mixing. Optical path length is 10 mm. [PicCl]$_b$ = 42 μM, [Na$_2$SO$_3$]$_b$ = 5.50 mM. (A) 1 min., (B) 3 min., (C) 5 min., (D) 10 min., (E) 25 min.

duct (IV); chemical shifts (δ), in water relative to internal TMS$^b$, 5.10 (d 1H), 8.35 (d 1H).

The initial rapid development of optical density at 460 nm and its disappearance are shown in Fig. 1. The value of (ΔOD)$_t$, which is defined as the difference between maximum optical density in Fig. 1 and that at $t=0$ on the oscilloscope trace, is plotted against wavelength in the range 350-600 nm in Fig. 2. There is a peak at 460 nm and broad absorption in the lower energy region ~525 nm. This spectrum may be taken as the true absorption spectrum, because the dead time in the stopped-flow apparatus was kept constant throughout the experiment. Kinetic measurements on the formation of the initial complex were carried out in the range 420-540 nm. The observed rate constants, $k_{obs}$, are given in Table 1 and independent of wavelength within the experimental error. Hence, the spectrum in Fig. 2 can be attributed to one species.

The anionic complex is, in general, stabilized in a solution containing DMSO. The absorption spectra of the mixture of PicCl (42 μM) and sodium sulphite (5.5 mM) in 1:1 v/v DMSO-H$_2$O at various times are shown in Fig. 3. The initial spectrum (A) is quite similar to that of Fig. 2. Because

16 As tetramethylsilane is insoluble in water, these chemical shifts were measured relative to internal dioxane, assuming a difference of 3.70 ppm between the two standard. See R. A. Y. Jones, A. R. Katritsky, J. N. Murrell and N. Sheppard, J. Chem. Soc., 2576 (1962)
The Intermediate in the Reaction between Picryl Chloride and Sodium Sulphite

The transient species has a short life in aqueous solution, and the solubility of sulphite ion in aqueous DMSO is low, the NMR spectrum of the transient could not be obtained. The position of the absorption maximum is independent of the concentration of sodium sulphite. While the absorption spectrum is not diagnostic of 1, 1- or 1, 3-σ-complex, the similarity of the shape of the present spectrum with that of 1, 3-σ-complex between PicCl and \( \text{CH}_3\text{O}^- \), in which \( \lambda_{\text{max}} = 424 \) and \( 475 \text{ nm} \), suggests that the initial complex is V rather than VI. The present spectrum shows red shift in comparison with that of PicCl and \( \text{CH}_3\text{O}^- \) system probably because of higher degree of solvation of divalent anion than univalent one.

\[
\text{PicCl} + \text{SO}_3^{2-} \xrightleftharpoons[k_1]{k_{-1}} V
\]

\[
k_{\text{obs}}(1) = k_1[\text{SO}_3^{2-}]_0 + k_{-1}
\]

Fig. 4 Observed first order rate constant, \( k_{\text{obs}}(1) \), as a function of [Na\(_2\)SO\(_4\)]\(_0\) at various temperatures. \( \bullet \): \( \mu \) (ionic strength) = 0.06 M at 25.0°C, \( \Delta \): \( \mu = 0.15 \) M at 25.0°C. The others were not measured at constant ionic strength.

The kinetics of the initial rapid reaction to form V, during which the subsequent reaction can be ignored, obeyed the first-order rate equation. The observed rate constant, \( k_{\text{obs}}(1) \), is related to the specific rate constants, \( k_1 \) and \( k_{-1} \) and the concentration of \( \text{SO}_3^{2-} \) by equation (2), taking reaction (1) into consideration. The relationships are shown in Fig. 4 where all experimental points were measured at 460 nm. The accuracy of each rate constant of the present study is less than 5%. There appears to be no significant effect of ionic strength in the range 0.06–0.15 M. A similar insensitivity of the rate constants to the ionic strength was also found for the formation of other anionic \( \sigma \)-complexes\(^9,10,12\) and is well understood as the reaction takes place between a neutral molecule and an ion.
Disappearance of initial complex

The final product after long standing of the mixture of PicCl and sodium sulphite was IV as identified by NMR and absorption spectra\(^\text{13}\). The decrease of the optical density at 460nm due to the formation of IV also obeyed well the first order rate equation. The contribution to the optical density due to IV was slight\(^\text{13}\) and neglected in this study. The observed first-order rate constant, \(k_{\text{obs}(2)}\), was independent of ionic strength and was related to the initial \(\text{SO}_3^{2-}\) concentration as shown in Fig. 5. Increasing the \(\text{SO}_3^{2-}\) concentration, the rate of increase of \(k_{\text{obs}(2)}\) was made slow down. Which suggests that the rate-determining step does not include a secondary sulphite attack.

It seems likely, therefore, that the final product (IV) is formed through VI rather than V, according to the following reaction scheme. Two similar competitive reactions have been found in the reaction of 2, 4, 6-trinitroanisole (TNA) with \(\text{CH}_3\text{O}^{2-}\)\(^\text{2,3}\). The liberation of \(\text{Cl}^-\) in step (iii) may be fast\(^\text{17}\), and the disappearance of V is controlled by the formation VI. Equilibrium (iv) is considered to be maintained during the process of the disappearance of V\(^\text{13}\). The above kinetic process gives the relationship expressed by equation (3).

\[
k_{\text{obs}(2)} = \frac{k_1[\text{SO}_3^{2-}]_0}{1 + (k_1/k_2)[\text{SO}_3^{2-}]_0}
\]  

\( k_{\text{obs}(2)} \) as a function of \([\text{Na}_2\text{SO}_3]_0\) according to equation (3). Symbols represent the same as those in Fig. 5.
The Intermediate in the Reaction between Picryl Chloride and Sodium Sulphite

\[ \text{PicCl} + \text{SO}_3^- \xrightarrow{k_1} V \]

\[ \xrightarrow{k_2} \text{VI} \]

\[ \xrightarrow{(i)} \]

\[ \xrightarrow{(iii)} \]

\[ \xrightarrow{(iv)} \]

A plot of \( k_{\text{obs}}(2) \) against \( [\text{SO}_3^-]_0/(1+(k_1/k_2)[\text{SO}_3^-]_0) \) is shown in Fig. 6. The plot is linear within experimental error, and \( k_2 \) was determined from the slope.

The kinetic and thermodynamic parameters for the reaction of PicCl with \( \text{SO}_3^- \) are summarized in Table 2. The corresponding data for the reaction of TNB with \( \text{SO}_3^- \) and TNA with \( \text{CH}_3\text{O}^- \) are included for comparison. For all systems, the attack on a non-substituted carbon has relatively low equilibrium constant but high rate constant, while the attack on a substituted carbon is slow but has high equilibrium constant.

**Energetic consideration**

Strauss has suggested that \( \text{SO}_3^- \), as it is doubly charged, should be much more strongly solvated than \( \text{CH}_3\text{O}^- \) or \( \text{CN}^- \) is, so that the steric hindrance to attack on a ring-substituted position will be severe\(^{17}\)). However, \( \Delta S^\dagger \) for \( \text{SO}_3^- \) or \( \text{CH}_3\text{O}^- \) attack on a non-substituted position is similar to that for attack on a substituted position, and so this suggestion is not correct. The difference in the rates

**Table 2  Kinetic and thermodynamic parameters of α-complex formation reactions at 25.0°C**

<table>
<thead>
<tr>
<th>( k_1 (M^{-1} \text{sec}^{-1}) )</th>
<th>( k_{-1} ) (sec(^{-1}))</th>
<th>( K (M^{-1}) )</th>
<th>( \Delta H^\circ (\text{kcal mol}^{-1}) )</th>
<th>( \Delta S^\circ (\text{e. u.}) )</th>
<th>( \Delta S^\dagger (\text{e. u.}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3.7 \times 10^4 ) ( (5.08 \pm 0.25) \times 10^4 )</td>
<td>115</td>
<td>( 3.2 \times 10^6 )</td>
<td>( 78.9 \pm 9.8 )</td>
<td>( -12.5 \pm 2.3 )</td>
<td>( -12.9 \pm 1.7 )</td>
</tr>
<tr>
<td>( 9.3 \times 10^4 )</td>
<td>300</td>
<td>( )</td>
<td>( 78.9 \pm 9.8 )</td>
<td>( -12.5 \pm 2.3 )</td>
<td>( -12.9 \pm 1.7 )</td>
</tr>
<tr>
<td>( 1.03 \times 10^{-3} )</td>
<td>( 1.70 \times 10^4 )</td>
<td>( 1.03 \times 10^{-3} )</td>
<td>( 1.70 \times 10^4 )</td>
<td>( 1.03 \times 10^{-3} )</td>
<td>( 1.70 \times 10^4 )</td>
</tr>
</tbody>
</table>

\(^a\)Ref. 12, \(^b\)Present work, \(^c\)Ref. 8, \(^d\)k in equation (3).

\(^{17}\) J. Miller, J. Amer. Chem. Soc., 85, 1628 (1963)
of reaction to give 1, 1- and 1, 3-σ-complexes is mainly due to $\Delta H_{\text{a}}^{\neq}$. Either methoxy or chloro substituent on the C$_1$-position seems to restrain the formation of the σ-complex, perhaps because the electronegmetric effects of these groups increase the electronic density at the reaction site.

Miller's semiempirical approach to nucleophilic aromatic substitution has often proved successful in explaining the reactivities of univalent nucleophiles, despite a number of assumptions inherent in the calculations. In the present case, reliable data for the electronegativity and the hydration energy of SO$_3^{2-}$ are not known. Moreover, the desolvation energy of a divalent ion, $V$ or $VI$, may be different from that of an univalent ion, e.g., $I$ or $II$, which Miller supposed approximately equal to the heat of hydration of the picrate ion. Although conscious of these deficiencies, the author attempted to consider the reactivities as to the formation and the decomposition of $V$ and $VI$, following Miller's approach. On the basis of the experimentally determined change of the enthalpy of decomposition of $V$, i.e., +3.6 kcal mole$^{-1}$, the energy of activation $\Delta H_{\text{a}}^{\neq}$ was estimated. The dissociation energy of the C-S bond is 62-70 kcal mole$^{-1}$, and so $\Delta H_{\text{a}}^{\neq}$ is calculated to be 16-18 kcal mole$^{-1}$ according to the curve relating the fraction of bond dissociation energy with the degree of thermicity derived by Miller. The enthalpy change for the liberation of SO$_3^{2-}$ from $VI$ is probably similar to that for the liberation from $V^{17}$. While, $\Delta H_{\text{a}}^{\neq}$ for $VI$ may be less than that for $V$ by the amount of σ-substituent effect, though its numerical value is not known. In the range of present consideration, the energy profile can be drawn as Fig. 7. Thus the semiempirical calculation predicts that the formation of $VI$ will be kinetically more favored than $V$. However, it is remarkably inconsistent with the experimental results. The similar discrepancy between the calculated and the observed reactivities was also found in the reaction of TNA with CH$_3$O$^{-2,3}$. A substituent at C$_1$-position which will only slightly affect the electronic spectrum of 1:1 σ-complex will exert remarkable influences upon the reactivities of both the 1, 1- and 1, 3-σ-complexes. This appears to be an important subject remaining with this semiempirical method of calculation.

**Fig. 7** Energy profile in the reaction of PicCl with SO$_3^{2-}$ in aqueous solution (in kcal mole$^{-1}$).

---: experimental. ---: calculated.

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19) Figure 5 in Reference 17