THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 45, NO. 1, 1975

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_3-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-H_2O 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 C_1-position and C_3-position take place concurrently and the former may be accompanied with higher energy barrier.

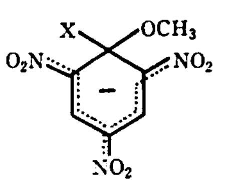
Introduction

1-X-2, 4, 6-Trinitrobenzene (X=OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$) can react with nucleophiles such as CH_3O^- 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=OCH_3) and CH_3O^- in methanol-DMSO, first by Servis by NMR[2]. There are also spectroscopic and kinetic evidences for the same thing in methanol by Bernasconi[3]. There are several spectroscopic and kinetic studies on the reaction of substituted dinitrobenzenes and trinitrobenzenes with CH_3O^- in methanol or methanol-DMSO[4~8].

(*Received May 26, 1975*)

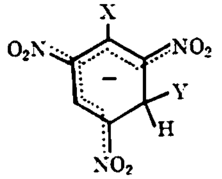
* Present address: Department of Chemistry, Faculty of Science, Kyoto Universiry, Kyoto, Japan.

1) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970)
2) K. L. Servis, *J. Amer. Chem. Soc.*, **87**, 5495 (1965), *ibid.*, **89**, 1508 (1967)
3) C. F. Bernasconi, *J. Amer. Chem. Soc.*, **93**, 6975 (1971)
4) F. Terrier and F. Millot, *Bull. Soc. Chim. France*, 1743 (1970)
5) F. Millot and F. Terrier, *Bull. Soc. Chim. France*, 2692 (1969)
6) R. Gaboriaud and R. Schaal, *Bull. Soc. Chim. France*, 2683 (1969)
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)



I

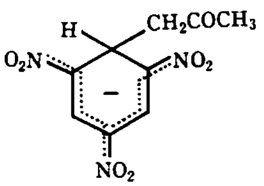
($X=H$, CH_3O)



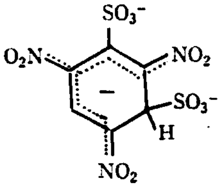
IIa: $Y=CH_3O$,
IIb: $Y=SO_3^-$

II

($X=H$, CH_3O, NH_2, $NH(CH_3)$, $N(CH_3)_2$)



III



IV

On the other hand, it was found by NMR that 1-X-2, 4, 6-trinitrobenzenes react with SO_3^{2-} to form only stable 1, 3-σ-comlpex (IIb) in low concentration of SO_3^{2-} in DMSO-H_2O 9,10). The reaction of picryl chloride with acetonate ion also gives only 1, 3-σ-complex (III) 11). The reactions of 2, 4, 6-trinitrobenzene (TNB) and 1-substituted-TNB with SO_3^{2-} were kinetically studied in aqueous solution 12~14). There are some papers concerned with the reaction of picryl chloride (PicCl) with anionic nucleophiles such as OH^- and CH_3O^- 6). The interpretation to attribute the transient colored species to 1, 1-σ-complex was criticized 1,15), because chloride ion is, in general, a better leaving group than OH^- or CH_3O^-.

In this paper the reaction of PicCl with SO_3^{2-} was studied from the view point 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

---

9) M. R. Crampton, *J. Chem. Soc.* (*B*), 1341 (1967)
10) A. R. Norris, *Can. J. Chem.*, 45, 175 (1967)
11) R. Foster, C. A. Fyfe, P. H. Emslie and M. I. Foreman, *Tetrahedron*, 23, 227 (1967)
12) M. Sasaki, *Chem. Letters*, 205 (1973)
13) M. Sasaki, *This Journal*, 43, 44 (1973)
14) E. Buncell, A. R. Norris, K. E. Russell and P.J. Sheridan, *Can. J. Chem.*, 52, 25 (1974)
15) L. H. Gan and A. R. Norris, *Can. J. Chem.*, 52, 18 (1974)

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 2 mm 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.* 1 mM, was mixed with sodium sulphite in the range 5–10 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[13]. This compound is the 1 : 1 ad-

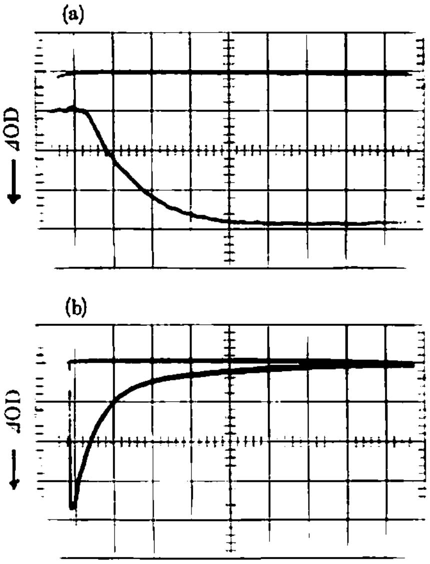


Fig. 1 Representative stopped-flow traces at 460 nm at 25.0°C. $[\mathrm{PicCl}]_0 = 80\ \mu$M, $[\mathrm{Na_2SO_3{}^{2-}}]_0 = 20$ mM. Vertical scale: ΔOD/div = 0.02. Horizontal scale: (a) 5 msec/div, (b) 500 msec/div. An upper line shows a flow signal.

Table 1 Observed first-order rate constant, $k_{obs(1)}$, for the formation of the initial complex between PicCl (41 μM) and sodium sulphite (3.4 mM) at 25°C.

wavelength, nm	$k_{obs(1)}$, sec^{-1}
420	80.5
440	75.5
460	78.8
480	76.0
500	74.0
520	75.1
540	79.0

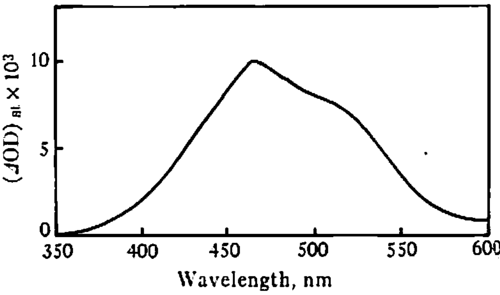


Fig. 2 Stopped-flow spectrum of the initial complex (V) in aqueous solution at 25.0°C. $[PicCl]_0$= 41 μM. $[Na_2SO_3]_0$=3.42 mM. Optical path length is 2 mm.

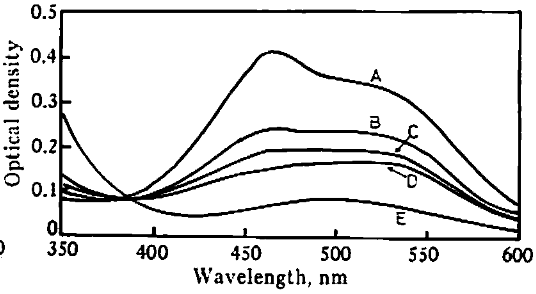


Fig. 3 Visible absorption spectra of the initial transient in DMSO-H_2O (1 : 1 v/v) at the following time after mixing. Optical path length is 10 mm. $[PicCl]_0$=42 μM, $[Na_2SO_3]_0$ =5.50 mM. (A) 1 mim., (B) 3 min., (C) 5 min., (D) 10 min., (E) 25 min.

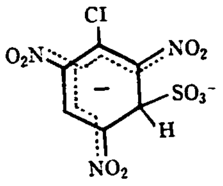
duct (IV); chemical shifts (δ), in water relative to internal TMS[16], 5.10 (d 1H), 8.35 (d 1H).

The initial rapid development of optical density at 460 nm and its disappearance are shown in Fig. 1. The value of $(\Delta OD)_{st}$, 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, $k_{obs(1)}$, 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.

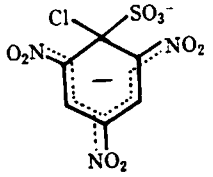
The anionic complex is, in general, stabilized in a solution containing DMSO. The absorption spectra of the mixture of PicCl (42 μM) and sodium sulphite (5.5 mM) in 1 : 1 v/v DMSO-H_2O at various times are shown in Fig. 3. The initial spectrum (A) is quite similar to that of Fig. 2. Because

---

[16] As tetramethylsilane is insoluble in water, these chemical shifts were measured relative to internal dioxane, assuming a diffrence of 3.70 ppm between the two standard. See R. A. Y. Jones, A. R. Katritzky, J. N. Murrell and N. Sheppard, *J. Chem. Soc.*, 2576 (1962)



V



VI

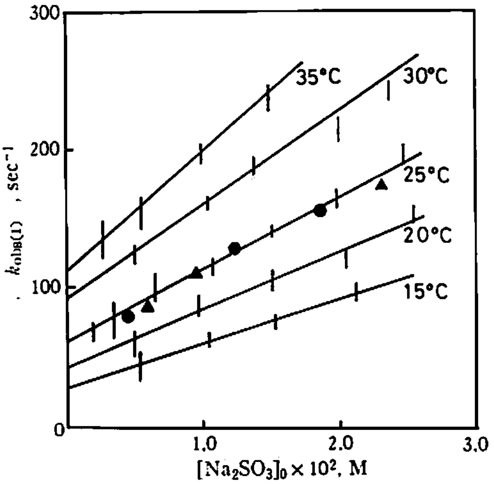


Fig. 4 Observed first order rate constant, $k_{obs(1)}$, as a function of $[Na_2SO_3]_0$ at various temperatures. ●: μ (ionic strength) = 0.06 M at 25.0°C, ▲: μ=0.15 M at 25.0°C. The others were not measured at constant ionic strength.

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 similality of the shape of the present spectrum with that of 1, 3-σ-complex between PicCl and CH_3O^-, in which λ_{max}=424 and 475 nm[15], suggests that the initial complex is V rather than VI. The present spectrum shows red shift in comparison with that of PicCl and CH_3O^- system probably because of higher degree of solvation of divalent anion than univalent one.

$$PicCl + SO_3^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V \qquad (1)$$

$$k_{obs(1)} = k_1[SO_3^{2-}]_0 + k_{-1} \qquad (2)$$

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, $k_{obs(1)}$, is related to the specific rate constants, k_1 and k_{-1} and the concentration of 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 460nm. 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 σ-complexes[9,10,12] and is well understood as the reaction takes place between a neutral molecule and an ion.

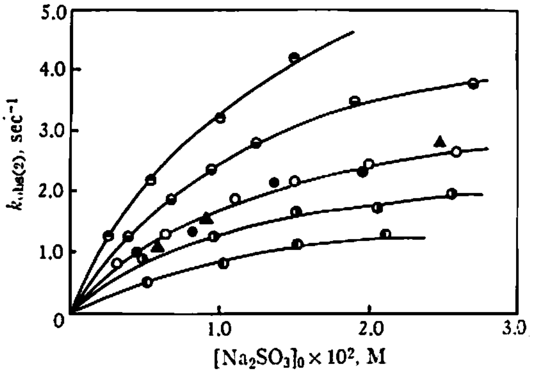


Fig. 5 The dependence of observed first-order rate constant, $k_{obs(2)}$, on $[Na_2SO_3]_0$ at various temperatures.
◐: 15.0°C, ◑: 20.0°C, ○: 25.0°C,
◒: 30.0°C, ◓: 35.0°C,
●: μ=0.06 M at 25.0°C,
▲: μ=0.15 M at 25.0°C.

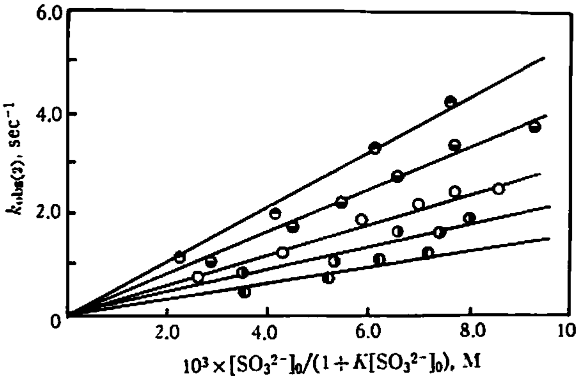


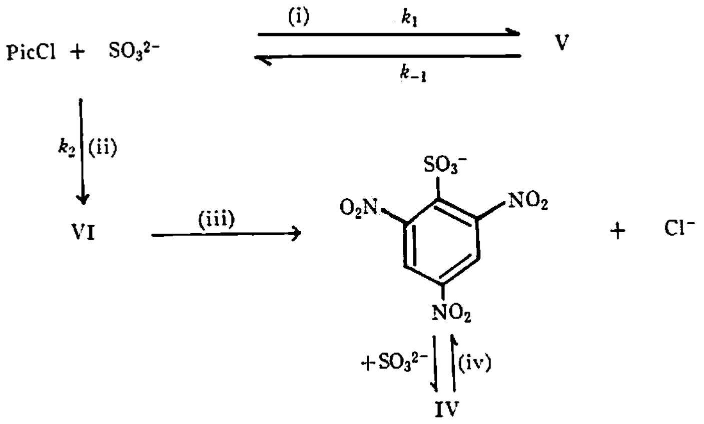
Fig. 6 $k_{obs(2)}$ as a function of $[Na_2SO_3]_0$ according to equation (3). Symbols represent the same as those in Fig. 5.

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[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[13] and neglected in this study. The observed first-order rate constant, $k_{obs(2)}$, was independent of ionic strength and was related to the initial SO_3^{2-} concentration as shown in Fig. 5. Increasing the SO_3^{2-} concentration, the rate of increase of $k_{obs(2)}$ 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 CH_3O^-[2,3]. The liberation of Cl^- in step (iii) may be fast[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[13]. The above kinetic process gives the relationship expressed by equation (3).

$$k_{obs(2)} = \frac{k_2[SO_3^{2-}]_0}{1+(k_1/k_{-1})[SO_3^{2-}]_0} \qquad (3)$$



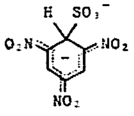
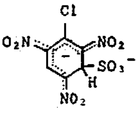
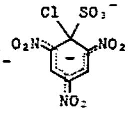
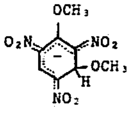
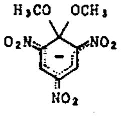
A plot of $k_{obs(2)}$ against $[SO_3^{2-}]_0/\{1+(k_1/k_{-1})[SO_3^{2-}]_0\}$ is shown in Fig. 6. The plot is linear within experimental error, and k_2 was determined from the slope.

The kinetic and thermodynamic parameters for the reaction of PicCl with SO_3^{2-} are summarized in Table 2. The corresponding data for the reaction of TNB with SO_3^{2-} 12) and TNA with CH_3O^- 3) 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 SO_3^{2-}, as it is doubly charged, should be much more strongly solvated than CH_3O^- or CN^- is, so that the steric hindrance to attack on a ring-substituted position will be severe1). Howerer, $\Delta S_1^{\ddagger}$ for SO_3^{2-} or CH_3O^- 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 σ-complex formation reactions at 25.0°C

	 in H_2O^a	 in H_2O^b	 in H_2O^b	 in CH_3OH^c	 in CH_3OH^c
$k_1(M^{-1}\,sec^{-1})$	3.7×10^4	$(5.08\pm0.25)\times10^3$	300^d	950	17.3
$k_{-1}(sec^{-1})$	115	64.4 ± 3.2	small	350	1.03×10^{-3}
$K(M^{-1})$	3.2×10^2	78.9 ± 9.8	large	2.71	1.70×10^4
$\Delta H_1^{\ddagger}$(kcal mol⁻¹)	7.5 ± 0.8	8.6 ± 0.7	10.1 ± 1.2	10.4 ± 1.0	12.9 ± 1.0
$\Delta H_{-1}^{\ddagger}$(kcal mol⁻¹)	11.4 ± 1.0	12.2 ± 1.2		8.2 ± 0.5	18.4 ± 1.0
ΔH°(kcal mol⁻¹)	-3.9 ± 1.8	-3.6 ± 1.9		2.2 ± 1.5	-5.5 ± 2.0
$\Delta S_1^{\ddagger}$(e. u.)	-12.6 ± 1.8	-12.9 ± 1.7	-12.5 ± 2.3	-10.8 ± 3.4	-9.4 ± 3.4
$\Delta S_{-1}^{\ddagger}$(e .u.)	-11.4 ± 3.4	-9.6 ± 3.0		-19.3 ± 1.7	-4.8 ± 3.4
ΔS°(e. u.)	-1.2 ± 5.2	-3.3 ± 4.7		8.5 ± 5.1	-4.6 ± 4.0

[a]Ref. 12, [b]Present work, [c]Ref. 8, [d]k_2 in equation (3).

---

17) J. Miller, *J. Amer. Chem. Soc.*, **85**, 1628 (1963)

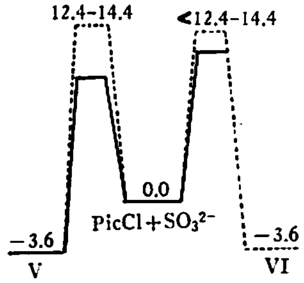


Fig. 7 Energy profile in the reaction of PicCl with SO_3^{2-} in aqueous solution (in kcal $mole^{-1}$).
—— : experimental, - - - : calculated.

of reaction to give 1, 1- and 1, 3-σ-complexes is mainly due to $\Delta H_1^{\ddagger}$. Either methoxy or chloro substituent on the C_1-position seems to restrain the formation of the σ-complex, perhaps because the electrometric 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 a 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 $\Delta H_{-1}^{\ddagger}$ was estimated. The dissociation energy of the C-S bond is 62–70 kcal $mole^{-1}$ [18], and so $\Delta H_{-1}^{\ddagger}$ 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[19]. The enthalpy change for the liberation of SO_3^{2-} from VI is probably similar to that for the liberation from V[17]. While, $\Delta H_{-1}^{\ddagger}$ for VI may be less than that for V by the amount of α-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_3O^- [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.

Department of Chemistry,
College of Liberal Arts and Science,
Kyoto University,
Kyoto, Japan

---

[18] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworth Scientific Publication, London, 1958, Table 11. 5. 1.

[19] Figure 5 in Reference 17