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A Kinetic Study on Reduction of 9,9′-Bifluorenylidene by Sodium Isopropoxide

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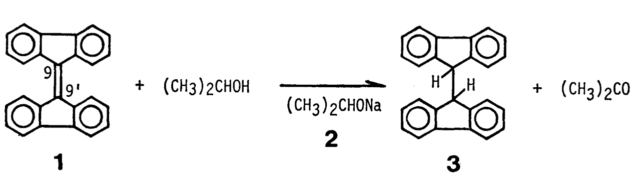
The kinetics and mechanism of reduction of 9,9′-bifluorenylidene (**1**) by sodium isopropoxide (**2**) in isopropyl alcohol to yield 9,9′-bifluorenyl (**3**) were investigated spectrophotometrically. The kinetic data suggest that the reduction proceeds autocatalytically, the reduction product **3** acting as the catalyst. It was found that

$$\mathbf{1} \xrightarrow[\mathbf{2}]{k_1} \mathbf{3} \qquad (1) \qquad\qquad \mathbf{1} + \mathbf{3} \xrightarrow[\mathbf{2}]{k_2} \mathbf{3} + \mathbf{3} \qquad (2)$$

Reactions 1 and 2 are of the first order with respect to **1**, but that the former is of the third order with respect to **2**, whereas the latter is of the first. The fourth- and third-order rate constants, k_1 and k_2, for Reactions 1 and 2 were determined to be 3.0×10^{-5} dm^9 mol^{-3} s^{-1} and 1.1×10^{3} dm^6 mol^{-2} s^{-1}, respectively, at 130 °C. Probable mechanisms for Reactions 1 and 2 have been offered on the basis of the reaction order for each molecular species involved.

Obviously, the symmetry of the fulvalene system demands that the central double bond has no dipole moment; however, it would also be expected that it has unusual properties.$^{1)}$ Indeed, the bond index of that linkage is very low for a double bond and, taking 9,9′-bifluorenylidene (**1**) as an example, the linkage has an unusually high polarizability, which results in various interesting results: *e.g.*, a large molecular refraction$^{2)}$ and an unusually low reduction potential.$^{3-5)}$ Among the unusual reactions of fulvalenes, the reduction of the central double bond by sodium alkoxides may be a typical example, since the C=C double bond is, in general, not reducible by such weak reductants.$^{6)}$ In the previous work$^{7)}$ it was found that **1** is readily reduced by sodium ethoxide and gives 9,9′-bifluorenyl (**3**). In order to elucidate this mechanism, a kinetic study on reduction of **1** by sodium isopropoxide (**2**) in isopropyl alcohol (Scheme 1) has been made. Sodium isoproxide was chosen as an alkoxide because its oxidation product was acetone, which did not lead to any side reaction, and, in addition, the sequence of the reduction rate of **1** by alkoxide was methoxide<ethoxide<isopropoxide.$^{8)}$



Scheme 1.

Experimental

Reduction of **1** *by Sodium Isopropoxide.* Metallic sodium (0.23 g, 1.0×10^{-2} g-atom) was treated with 5 ml of isopropyl alcohol; the resulting solution was transferred into a glass tube. Then 0.17 g (5.2×10^{-4} mol) of **1** was added. The glass tube was sealed and heated at 130 °C in an oil bath until the orange-red color of the solution disappeared completely. After cooling, the content was poured into water and extracted with benzene–ether (1:1). The solvent was evaporated. Recrystallization of the residue from benzene gave **3**, 0.16 g (93%); mp 245 °C. This compound was identified by direct comparison with an authentic sample. On the other hand, when the chemical components in the distillate from the reduction mixture were analyzed by gas chromatography, acetone was found.

Stock Solutions of 1 and 3. Compounds **1** and **3** were dissolved separately in isopropyl alcohol to a concentration of 2×10^{-3} mol dm^{-3}. These solutions were stored in a dark room and were stable for at least a month. Each solution was diluted with isopropyl alcohol as required for experiments.

Kineitc Measurements. Red compound **1** has an absorption spectrum in the visible region, with its maxium absorbance at 458 nm and with the molar absorptivity of 2.13×10^{4} dm^3 mol^{-1} cm^{-1}, probably attributable to a π-π^* electronic transition, while **3** shows no visible absorption spectrum. The decrease in the absorbance due to the reduction of **1** was a function of the time when measured spectrophotometrically. A required amount of isopropyl alcohol solution of **2** and 2.5 ml of 2×10^{-4} mol dm^{-3} solution of **1** were taken in a 25 ml volumetric flask and diluted with isopropyl alcohol up to the mark. A 5 ml of the aliquot was transferred into a glass tube, 11 mm in external diameter and about 100 mm high, which was used as both a reaction vessel and a spectrophotometric cell.$^{9)}$ The tube was sealed and then immersed in an oil bath thermostated at 130 °C within an accuracy of 0.2 °C. The oil bath was covered with aluminium foil to prevent any effect of light on the reaction. The absorbance at 458 nm was measured at a given interval (at least 10 min) with a Shimadzu SP-20 spectrophotometer, after taking out the glass tube and wiping off the oil which had stuck on its outside surface. Another glass tube of the same size and quality containing isopropyl alcohol was used as the reference during the spectrophotometry.

Results

The reduction rate of **1** by **2** was measured at 130 °C for various concentrations of **2** (6×10^{-3} to 1.4×10^{-1} mol dm^{-3}) under a constant concentration of **1** (2×10^{-5} mol dm^{-3}). The dimensionless quantity X as a function of the time t was plotted in Fig. 1, where $X=[\mathbf{1}]/[\mathbf{1}]_0$: $[\mathbf{1}]_0$ and $[\mathbf{1}]$ denote the concentrations of **1** at the initial time and at the time of measurement. The reduction for all the cases did not proceed appreciably at the initial stage and only began to proceed after some inductive period; the more the reduction proceeded, the greater the rate became, as seen in Fig. 1. Such behavior of X *vs.* t is frequently observed in the autocatalytic reactions such are as found in the acid-catalyzed hydrolyses of various esters and in various biochemical processes.[10,11]

A kinetic model of conversion from A to B which proceeds by an autocatalytic reaction in addition to the direct conversion would be:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B}, \tag{1a}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{B} + \mathrm{B}. \tag{1b}$$

If the concentrations of the molecular species A at the start and at the measurement time are denoted by A_0 and $A(t)$ and if Reactions 1a and 1b are both of the first order with respect to each substrate, the dimensionless quantity, $X_A(t)=A(t)/A_0$. and the rate, $-\mathrm{d}X_A(t)/\mathrm{d}t$, can be formalized as[10,11]

$$X_A(t) = \frac{k_1+k_2A_0}{k_1e^{(k_1+k_2A_0)t}+k_2A_0}, \tag{2}$$

$$-\frac{\mathrm{d}}{\mathrm{d}t}X_A(t) = \frac{k_1(k_1+k_2A_0)^2e^{(k_1+k_2A_0)t}}{[k_1e^{(k_1+k_2A_0)t}+k_2A_0]^2}. \tag{3}$$

In the above equations, k_1 and k_2 are the first- and second-order rate constants for Reactions 1a and 1b, respectively. The rate reaches its maximum at a particular time, t^*, which satisfies the equation, $\mathrm{d}^2X_A(t)/\mathrm{d}t^2=0$ *i.e.*,

$$k_1e^{(k_1+k_2A_0)t^*} = k_2A_0, \tag{4}$$

when $k_2A_0 \gg k_1$, Approximations 5 to 7 will be derived from the combination of Eqs. 2 to 4.

$$X_A(t^*) \simeq \frac{1}{2}, \tag{5}$$

$$-\frac{\mathrm{d}}{\mathrm{d}t}X_A(t^*) \simeq \frac{1}{4}k_2A_0, \tag{6}$$

$$k_1e^{k_2A_0t^*} \simeq k_2A_0. \tag{7}$$

Approximations 5 to 7 indicate that (i) the dimensionless quantity becomes equal to 1/2 when the conversion rate reaches its maximum, (ii) the k_2A_0 value is four times the slope of the tangential line at $t=t^*$ for the curve of $X_A(t)$ *vs.* t, and (iii) the k_1 value is obtainable with the use of Approximation 7 provided that the values of both t^* and k_2A_0 are known. All the curves of X *vs.* t measured for the reduction of **1** by **2** under the present conditions suggested that $k_2A_0 \gg k_1$, because the reduction rates were at their maximum when $X=1/2$, as seen in Fig. 1.

The apparent first- and second-order rate constants, k_1^{ap} and k_2^{ap}, for each concentration of **2** added were determined from the slope of the tangential line and from the time when $X=1/2$, with the use of Approximations 6 and 7, as indicated by a dashed line and an arrow for Curve 5 in Fig. 1: $k_1^{\mathrm{ap}}=2.4\times10^{-10}$ s^{-1} and $k_2^{\mathrm{ap}}=2.2\times10$ dm^3 mol^{-1} s^{-1} were obtained for $[\mathbf{2}]=2.0\times10^{-2}$ mol dm^{-3} from Curve 5. The $k_2^{\mathrm{ap}}A_0$ values determined were 3.8×10^4 to 2.1×10^7 times larger than the k_1^{ap} values over the concentration range of 1.4×10^{-1} to 6×10^{-3} mol dm^{-3} for **2**.

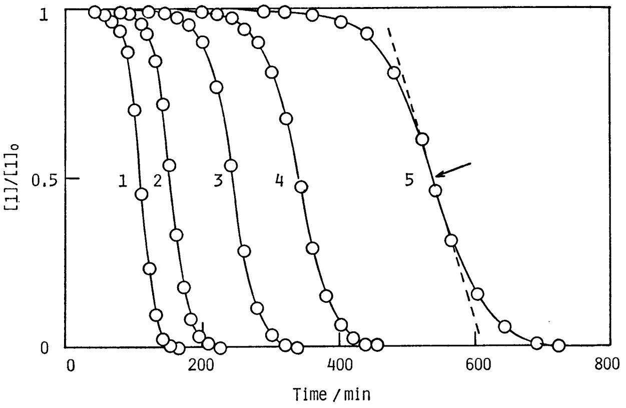


Fig. 1. Reduction of 9,9′-bifluorenylidene (**1**) by sodium isopropoxide (**2**) at 130 °C.
$[\mathbf{1}]_0$: 2.0×10^{-5} mol dm^{-3}. [**2**]: 1—8.0×10^{-2}, 2—6.0×10^{-2}, 3—4.0×10^{-2}, 4—3.0×10^{-2}, and 5—2.0×10^{-2} mol dm^{-3}.

As seen on the curves in Fig. 1, the inductive period in reduction becomes shorter with increase in the concentration of **2** added; in addition, the tangential line at the maximum rate becomes steeper, indicating that both k_1^{ap} and k_2^{ap} are dependent on the concentration of **2**. If Reactions 1a and 1b for the reduction of **1** are of the n- and m-th order with respect to **2**, the apparent first- and second-order rate constants, k_1^{ap} and k_2^{ap}, will be expressed by

$$k_1^{\mathrm{ap}} = k_1[\mathbf{2}]^n \quad \text{and} \quad k_2^{\mathrm{ap}} = k_2[\mathbf{2}]^m. \tag{8}$$

This is because **2** acts as the catalyst in this reaction and its concentration remains constant during the reaction. Plots of both $\ln k_1^{\mathrm{ap}}$ and $\ln k_2^{\mathrm{ap}}$ *vs.* ln [**2**] will give a straight line with each slope of n and m. Each linear plot with a slope of $n=3$ and $m=1$ in Figs. 2 and 3 suggests that Reaction 1a is of the third order and Reaction 1b is of the first order with respect to **2**. The values $k_1=3.0\times10^{-5}$ dm^9 mol^{-3} s^{-1} and $k_2=1.1\times10^3$ dm^6 mol^{-2} s^{-1} are obtained by extrapolating each linear part to ln $[\mathbf{2}]=0$.

Summarizing the foregoing discussion, we can say

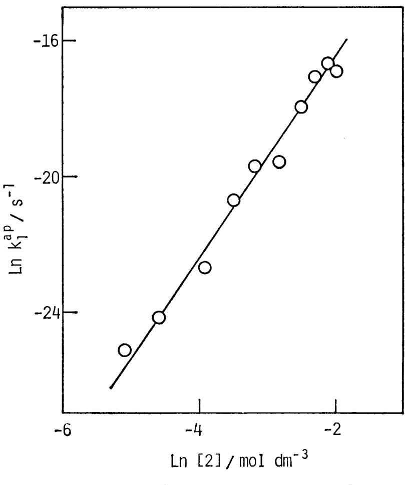


Fig. 2. Dependence of the apparent first-order rate constant, k_1^{ap}, on the concentration of sodium isopropoxide (**2**).

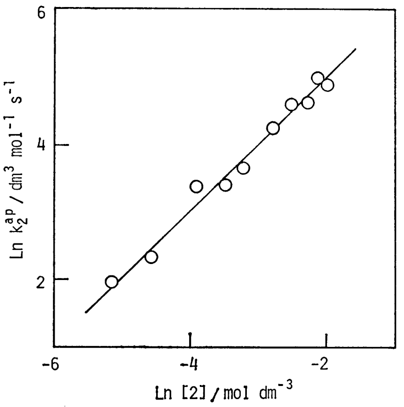


Fig. 3. Dependence of the apparent second-order rate constant, k_2^{ap}, on the concentration of sodium isopropoxide (**2**).

that the reduction of **1** by **2** in isopropyl alcohol to yield **3** proceeds by the following parallel reaction paths:

$$\mathbf{1} \xrightarrow[\mathbf{2}]{k_1} \mathbf{3}, \qquad (9a)$$

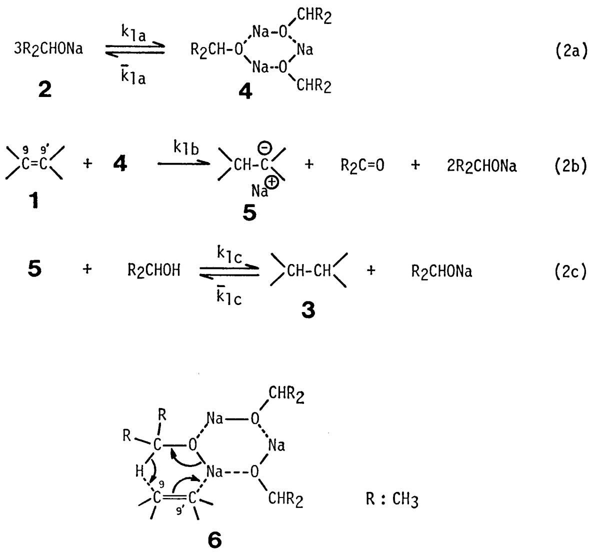
$$\mathbf{1} + \mathbf{3} \xrightarrow[\mathbf{2}]{k_2} \mathbf{3} + \mathbf{3}, \qquad (9b)$$

and its reduction rate is expressed by

$$-\frac{d}{dt}[\mathbf{1}] = k_1[\mathbf{2}]^3[\mathbf{1}] + k_2[\mathbf{2}][\mathbf{1}][\mathbf{3}]. \qquad (10)$$

Discussion

It is of interest to note that the reaction rate for Reaction 9a is of the third order with respect to **2**. High-order reactions regarding alkoxide are frequently observed in various reductions by alkoxide, *e.g.*, the second order in reduction of nitrobenzene by sodium methoxide,[12)] the first and second orders in benzophenone reduction by aluminium isopropoxide,[13)] and the third and forth orders in acetophenone reduction by aluminium isopropoxide.[14)] Such a high-order process regarding alkoxide is explaned by the association of alkoxide,[15)] and the transition-state complex is formed between the oxidant and the associated alkoxide.[16)] According to this interpretation, we offer Scheme 2 as a mechanism of Reaction 9a. The pre-equilibrium 2a between the monomer and trimer of **2** is supposed to exist. The trimer (**4**) reacts with **1** and the hydride ion from **4** is transferred to the C(9) or C(9′) atom of **1** to give an intermediate carbanion (**5**) (Step 2b), which will react readily with isopropyl alcohol to yield the final product **3** (Step 2c). Step 2b with a rate constant k_{1b} may be rate-determining: a transition-state complex with a six membered ring,[17,18)] as indicated in Formula **6**. Step 2c is in an equilibrium, as will be discussed later, which may shift strongly to the righthand side.



Scheme 2.

The reduction products of **1** by **2** in isopropyl alcohol were 9,9′-bifluorenyl **3** and acetone. Accordingly, one of these compounds is considered to act as the catalyst in this reaction. The reaction rate was measured in the presence of **3** or acetone. It was found that the reaction was remarkably accelerated in the presence of the former, but no effect was found for the latter. Figure 4 shows plots of X *vs.* t for the various initial concentrations of **3** when 2×10^{-5} mol dm^{-3} of **1** and 2×10^{-2} mol dm^{-3} of **2** were added. On the other hand, the dimensionless quantity $X_A(t)$ for the kinetic model (1) is expressed by Eq. 11, when the intial concentration of B (B_o) is not zero (see Appendix).

$$X_A(t) = \frac{k_1+k_2A_o+k_2B_o}{(k_1+k_2B_o)e^{(k_1+k_2A_o+k_2B_o)t}+k_2A_o} \qquad (11)$$

In the case of the reduction of **1** by **2**, k_1 and k_2 in the above equation will be replaced by $k_1[\mathbf{2}]^3$ and $k_2[\mathbf{2}]$, because Reactions 9a and 9b are found to be of the third and first orders with respect to **2**, which acts as the catalyst and keeps its concentration constant during the reaction. The X values for this reaction were calculated for the various initial concentrations of **3** on the basis of Eq. 11, with the use of the k_1 and k_2 values determined above. The experimental plots in Fig. 4 can be explained reasonably by the calculated values; this confirms that the reduction product **3** acts as the catalyst.

A catalytic reaction such as indicated by Scheme 3 is offered as a probable mechanism. Product **3** reacts with **2** to give an intermediate carbanion **5** (Step 3a), which is the reverse reaction of Step 2c. An electron transfer may take place from the carbanion **5** to the compound **1** to give 9-(9-fluorenyl)fluoren-9-yl radical (**8**) and its anion radical (**7**). The protonation of the anion radical **7** to give **8** may be in a rapid equilibrium (Step 3c). One molecule of the radical **8** may attack isopropyl alcohol and an α-hydrogen atom of the alcohol may be transferred to yield a final product **3** and an alcohol radical (**9**) (Step 3d). Another molecule of the radical **8** may react with the alcohol radical **9** produced in Step 3d to yield another molecule of the product **3** and acetone (Step 3e). Step 3b with an rate constant k_{2b} may be rate-determining, because (i) Equilibria 3a and 3c may be established very rapidly and (ii) each radical involved in the process may be very

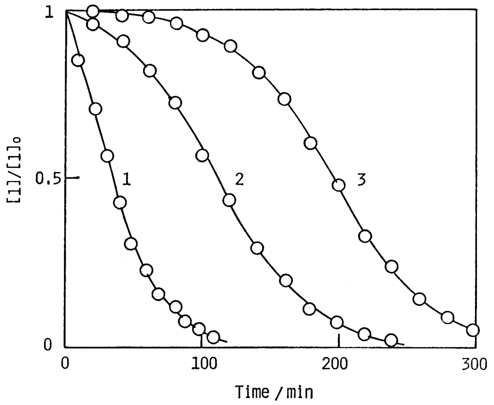
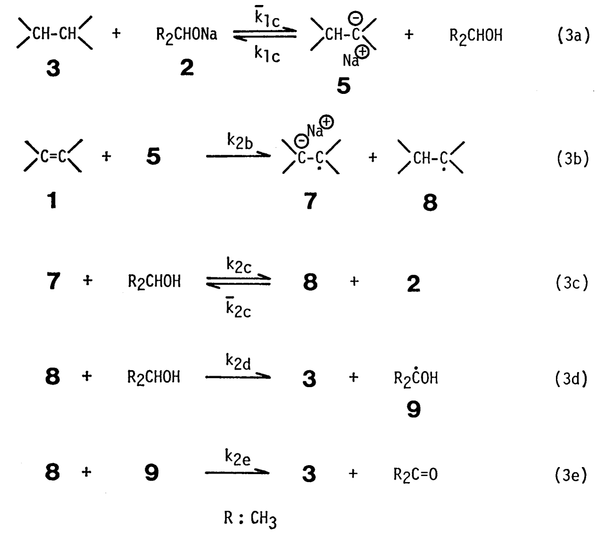


Fig. 4. Reduction of 9,9′-bifluorenylidene (**1**) by sodium isopropoxide (**2**) in the presence of added 9,9′-bifluorenyl (**3**) at 130 °C.
$[\mathbf{1}]_0$: 2.0×10^{-5} mol dm^{-3}. $[\mathbf{2}]$: 2.0×10^{-2} mol dm^{-3}. $[\mathbf{3}]_0$: 1—1.0×10^{-5}, 2—1.0×10^{-6}, and 3—1.0×10^{-7} mol dm^{-3}.



Scheme 3.

reactive.

If the autocatalytic reaction actually proceeds through the foregoing steps, some amount of the pinacol might be formed. This may be explained by that the dimerization of the alcohol radical **9** does not occur in alkaline media.[19,20] The existence of the radicals **7** to **9**, and also the kinetics of various 9,9′-bifluoreylidene derivatives, are now under investigation; we must await these results before giving a valid conclusion for the autocatalytic reaction.

Usually the C=C double bond is not reducible by sodium alkoxide. Regarding Compound **1**, two fluorene moieties are not on a plane, and the central C(9)=C(9′) double bond is twisted sterically.[21,22] Furthermore, despite the symmetry of the molecule, **1** has a considerably larger molar-polarization than expected.[2] This high distortion polarization is also reflected in the particular chemical reactivity of its central double bond; it is capable of adding an organometallic compound[23,24] and amines,[25] of reacting with lithium aluminium hydride,[26] and of undergoing the Michael condensation[27,28]—all reactions typical of high polar substances. Hydrogenation of this double bond by sodium isopropoxide **2** can be interpreted along the same line. However, the direct reduction of **1** by **2**, *i.e.*, Reaction 9a, proceeds very slowly even at 130 °C, as seen in the inductive period in Fig. 1. The most important factor in its reactivity with **2** is that the process involves the autocatalytic reaction 9b; the autocatalytic reaction proceeded 3.8×10^4 to 2.1×10^7 times rapidly as the direct reaction when 2×10^{-5} mol dm^{-3} of **1** and 1.4×10^{-1} to 6×10^{-3} mol dm^{-3} of **2** were reacted.

Appendix

If each process in the kinetic model (1) is of the first order with respect to each molecular species involved, the rate of change in the concentration of A with the time is given by

$$-\frac{\mathrm{d}}{\mathrm{d}t}A(t) = k_1A(t) + k_2A(t)B(t). \tag{A1}$$

The initial conditions for the above equation are:

$$A(0) = A_0 \quad \text{and} \quad B(0) = B_0. \tag{A2}$$

The total concentration of A and B at any time must satisfy the equation:

$$A(t) + B(t) = A_0 + B_0. \tag{A3}$$

Under the condition A3, Eq. A1 is rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}A(t) + (k_1+k_2A_0+k_2B_0)A(t) - k_2A^2(t) = 0. \tag{A4}$$

The differential equation A4 has the general solution A5:

$$A(t) = \frac{k_1+k_2A_0+k_2B_0}{Ce^{(k_1+k_2A_0+k_2B_0)t}+k_2}, \tag{A5}$$

where

$$C = \frac{K_1+K_2B_0}{A_0}. \tag{A6}$$

From Eqs. A5 and A6, $X_A(t)$ $[=A(t)/A_0]$ is derived as Eq. 9.

References

1) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).
2) E. D. Bergmann, E. Fisher, and J. H. Jaffe, *J. Am. Chem. Soc.*, **75**, 3230 (1953).
3) G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955).
4) G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, **74**, 277 (1955).
5) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. Ij. Aalbersberg, *Recl. Trav. Chim. Pays-Bas*, **73**, 355 (1954).
6) Y. Ogata, "Yukikagobutsu No Sanka To Kangen," Nankodo, Tokyo (1963), p. 758.
7) S. Kajigaeshi, S. Fujisaki, I. Aizu, and H. Hara, *Bull. Chem. Soc. Jpn.*, **52**, 3569 (1979).
8) Our unpublished data.
9) T. Yoshino, S. Murakami, H. Takesue, and M. Ishihara, *J. Inorg. Nucl. Chem.*, **42**, 579 (1980).
10) M. Boudart, "Kinetics of Chemical Process," Prentice-Hall, Englewood Cliffs (1968), p. 124.
11) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York (1961), p. 19.
12) Y. Ogata and J. Mibae, *J. Org. Chem.*, **27**, 2048 (1962).

13) W. N. Moulton, R. E. V. Atta, and R. R. Ruch, *J. Org. Chem.*, **26**, 290 (1961).
14) V. J. Shiner, Jr., and D. Whittaker, *J. Am. Chem. Soc.*, **85**, 2337 (1963).
15) V. J. Shiner, Jr., D. Whittaker, and V. P. Fernandez, *J. Am. Chem. Soc.*, **85**, 2318 (1963).
16) Y. Sawaki, "Koza Yukihannokiko 10: Sanka To Kangen Hanno (II)," ed by Y. Ogata, Tokyokagakudojin, Tokyo (1965), p. 286.
17) E. D. Williams, K. A. Krieger, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 2404 (1953).
18) H. Haubenstock and E. B. Davidson, *J. Org. Chem.*, **28**, 2772 (1963).
19) W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 391 (1933).
20) R. Tanikaga, "Shinjikkenkagakukoza 15: Sanka To Kangen [II]," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), p. 455.
21) N. A. Bailey and S. E. Hull, *J. Chem. Soc., D*, **1971**, 960.
22) H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.*, **97**, 2326 (1975).
23) R. C. Fuson and H. D. Porter, *J. Am. Chem. Soc.*, **70**, 895 (1948).
24) P. M. G. Bavin, *Can. J. Chem.*, **38**, 882 (1960).
25) L. A. Pink and G. E. Hilbert, *J. Am. Chem. Soc.*, **57**, 2398 (1935).
26) D. Lavie and E. D. Bergmann, *Bull. Soc. Chim. Fr.*, **1951**, 250.
27) K. Suzuki and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **37**, 1833 (1964).
28) K. Suzuki and S. Kajigaeshi, *Bull. Chem. Soc. Jpn.*, **35**, 408 (1962).