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A Kinetic Study on Denitration of 9,9′-Dinitro-9,9′-bifluorenyl by Tin(II) Chloride in *N,N*-Dimethylformamide

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(Received April 25, 1983)

Synopsis. The kinetics of the reductive elimination of nitro groups from 9,9′-dinitro-9,9′-bifluorenyl by tin(II) chloride in *N,N*-dimethylformamide (DMF) at 20 °C was investigated. It was found that the present elimination is a second-order reaction.

The potential usefulness of a radical anion-radical chain elimination reaction (E$_{\rm RC}$1) has been widely recognized.[1] Although numerous works have been published on the E$_{\rm RC}$1 of vicinal dinitro compounds,[2,3] α-cyano-β-nitro esters,[4] α-acetyl-β-nitro ketones,[5] and β-nitro sulfones,[6] little was known of their kinetics. The kinetic approach to the E$_{\rm RC}$1, in general, suffers from the drawbacks that the reaction system is heterogeneous, and that the reaction is carried out under the photoirradiation or at elevated temperatures. However, in the previous work[3] it was found that the denitration of α,β-diaryl vicinal dinitro compounds with tin(II) chloride in DMF proceeded readily at room temperature. Moreover, the E$_{\rm RC}$1 product from 9,9′-dinitro-9,9′-bifluorenyl (**1**) is 9,9′-bifluorenylidene (**2**), which has absorptions in the visible region probably attributable to a π-π* electronic transition. The large molar absorptivity of product **2** permits low concentrations of the reactants to be used, thus eliminating problems arising from the limted solubility of tin(II) chloride. Based on these preliminary findings, a kinetic study on *E*$_{\rm RC}$1 of **1** with tin(II) chloride in DMF has been made.

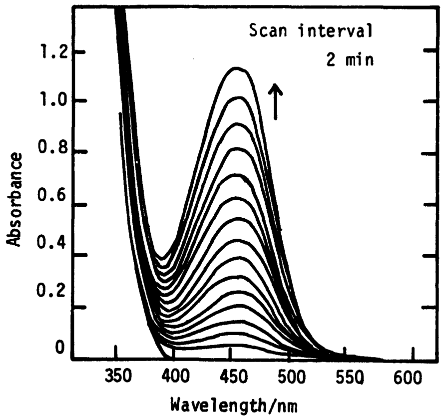


Fig. 1. Absorption spectral change due to the increase of 9,9′-bifluorenylidene (**2**) in the reaction of 9,9′-dinitro-9,9′-bifluorenyl (**1**) (2.73×10^{-3} mol dm^{-3}) with tin(II) chloride (1.86×10^{-2} mol dm^{-3}) in DMF at 20 °C.

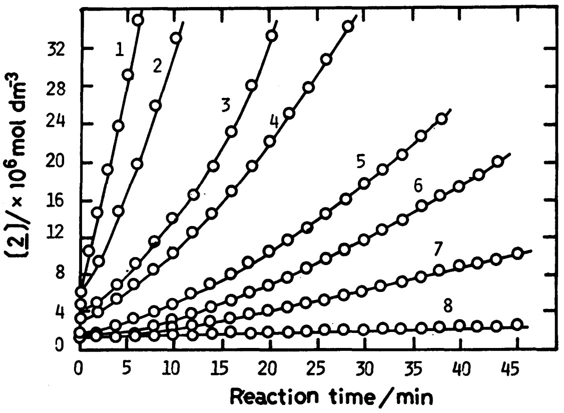


Fig. 2. Formation of **2** from **1** in a DMF solution at 20 °C.

The concentrations were as follows: 1, [**1**]$=9.50\times10^{-3}$ M and [SnCl$_2$]$=2.78\times10^{-2}$ M; 2, [**1**]$=5.68\times10^{-3}$ M and [SnCl$_2$]$=2.78\times10^{-2}$ M; 3, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=2.78\times10^{-2}$ M; 4, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=1.86\times10^{-2}$ M; 5, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=1.43\times10^{-2}$ M; 6, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=1.07\times10^{-2}$ M; 7, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=5.27\times10^{-3}$ M; 8, [**1**]$=2.73\times10^{-4}$ M and [SnCl$_2$]$=1.96\times10^{-3}$ M.

Experimental

Chemicals. Commercial anhydrous tin(II) chloride and DMF of the purest grade were used without further purification. Compound 1 was prepared according to the literature method.[3]

Procedure and Apparatus. The reaction of **1** with tin(II) chloride in DMF was initiated by the addition of the latter solution into a stirred solution of **1**, which was placed in the spectrophotometric cell (width 1 cm, quartz) immersed in a water bath thermostated at 20±0.1 °C. Red compound **2** has an extremely large absorptivity in DMF, $\varepsilon=2.30\times10^4$ dm^3 mol^{-1} cm^{-1} at 458 nm, while the other species in the reaction solution are transparent under the given concentrations. Consequently the absorbance of **2** formed was measured at an appropriate reaction time using a Hitachi Model 330 spectrophotometer.

Results and Discussion

A typical spectral change of the reaction mixture is shown in Fig. 1. Figure 2 shows a typical reaction profile. The concentrations used were 4.54×10^{-4}—9.5×10^{-3} mol dm^{-3} for **1** and 1.96×10^{-3}—2.78×10^{-2} mol dm^{-3} for tin(II) chloride. The runs were carried out to about 0.07—0.7% completion. For the reaction under consideration, we may write as follows:

$$r = \mathrm{d}[\mathbf{2}]/\mathrm{d}t = k[\mathbf{1}]^a[\mathrm{SnCl_2}]^b, \tag{1}$$

where *r*, [ ], *t*, *k*, *a*, and *b* denote the reaction rate, the concentration, the time, the rate constant, kinetic order with respect to **1**, and that with respect to tin(II) chloride, respectively. From Eq. 1, we get

$$\begin{aligned}\log r &= \log(\mathrm{d}[\mathbf{2}]/\mathrm{d}t)\\ &= \log k + a\log[\mathbf{1}] + b\log[\mathrm{SnCl_2}].\end{aligned} \tag{2}$$

Thus from measurements of the initial rate of the reaction in separate experiments, in which either of the reactants

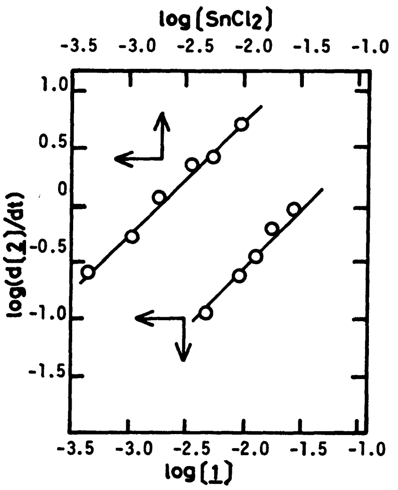


Fig. 3. log-log plots of the initial rate of the reaction of **1** with tin(II) chloride in DMF at 20 °C against the concentrations of **1** and tin(II) chloride.

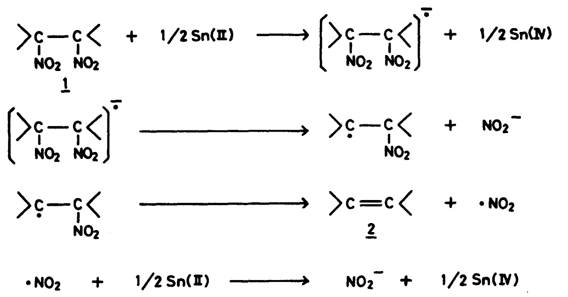
is kept constant, we may find orders *a* and *b*. Plots of both log [**1**] and log [$SnCl_2$] *vs.* og $r_{t\to 0}$ will give a straight line with each slope of *a* and *b*. Each linear plot with a slope of $a=1.00$ and $b=1.04$ in Fig. 3 suggests that the reaction rate is expressed by an equation

$$r = d[\mathbf{2}]/dt = k[\mathbf{1}]^{1.00}[SnCl_2]^{1.04} \qquad (3)$$

with a second-order constant $k=1.49\times10^4\ M^{-1}\ min^{-1}$ ($1\ M=1\ mol\ dm^{-3}$) at 20 °C. The net reaction is thus given by the following equation:

$$\mathbf{1} + Sn(II) \longrightarrow \mathbf{2} + Sn(IV) + 2\,NO_2^- . \qquad (4)$$

The mechanism of the present elimination appears to be one of the $E_{RC}1$[1] whose mechanism has been confirmed in the reaction of vicinal dinitro compounds or *β*-nitro sulfones with tributyltin hydride,[6] and the elimination seems to proceed according to the following reactions. By combining Eqs. 5—8 we obtain Eq. 4.



$$\underset{\mathbf{1}}{\underset{NO_2\ NO_2}{>C—C<}} + 1/2\,Sn(II) \longrightarrow \left[\underset{NO_2\ NO_2}{>C—C<}\right]^{\bar{\cdot}} + 1/2\,Sn(IV) \qquad (5)$$

$$\left[\underset{NO_2\ NO_2}{>C—C<}\right]^{\bar{\cdot}} \longrightarrow \underset{NO_2}{>\dot{C}—C<} + NO_2^- \qquad (6)$$

$$\underset{NO_2}{>\dot{C}—C<} \longrightarrow \underset{\mathbf{2}}{>C=C<} + \cdot NO_2 \qquad (7)$$

$$\cdot NO_2 + 1/2\,Sn(II) \longrightarrow NO_2^- + 1/2\,Sn(IV) \qquad (8)$$

The *k* value is *ca.* 7×10^5 times greater than the second-order rate constant for a similar reductive elimination of *meso*-stilbene dibromide with tin(II) chloride in DMF at 59.4 °C reported by Kwok and Miller.[7] It is also important to note that the *k* value is comparable to those for second-order electron transfer reactions among metal ions in liquid phase such as $Fe^{2+}+Co^{3+}\rightarrow Fe^{3+}+Co^{2+}$ at 0—25 °C.[8] The observed rate constant appears to be accounted for by the fact that the nitro group accepts most readily one electron among all the common functional groups.[6]

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