

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_{RC1}) has been widely recognized.¹⁾ Although numerous works have been published on the E_{RC1} 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_{RC1} , 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 work³⁾ 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_{RC1} 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 limited solubility of tin(II) chloride. Based on these preliminary findings, a kinetic study on E_{RC1} of **1** with tin(II) chloride in DMF has been made.

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, $\epsilon = 2.30 \times 10^4$ dm³ 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:

$$r = d[2]/dt = k[1]^a[\text{SnCl}_2]^b, \quad (1)$$

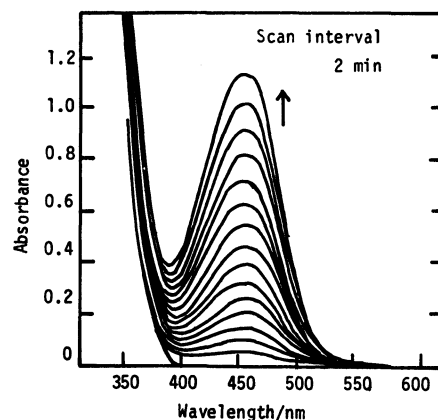


Fig. 1. Absorption spectral change due to the increase of 9,9'-bifluorenylidene (**2**) in the reaction of 9,9'-dinitro-9,9'-bifluorenyl (**1**) (2.73×10^{-3} mol dm⁻³) with tin(II) chloride (1.86×10^{-2} mol dm⁻³) in DMF at 20 °C.

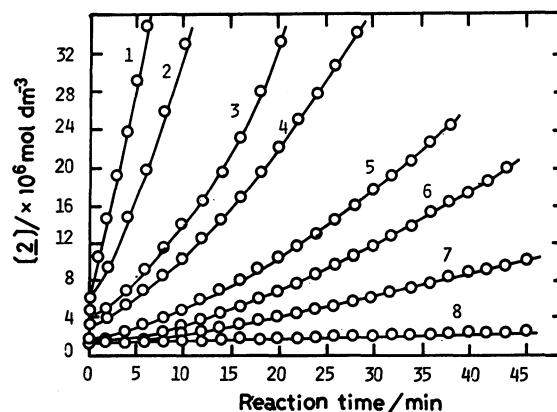


Fig. 2. Formation of **2** from **1** in a DMF solution at 20 °C.

The concentrations were as follows: 1, $[1] = 9.50 \times 10^{-3}$ M and $[\text{SnCl}_2] = 2.78 \times 10^{-2}$ M; 2, $[1] = 5.68 \times 10^{-3}$ M and $[\text{SnCl}_2] = 2.78 \times 10^{-2}$ M; 3, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 2.78 \times 10^{-2}$ M; 4, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 1.86 \times 10^{-2}$ M; 5, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 1.43 \times 10^{-2}$ M; 6, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 1.07 \times 10^{-2}$ M; 7, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 5.27 \times 10^{-3}$ M; 8, $[1] = 2.73 \times 10^{-4}$ M and $[\text{SnCl}_2] = 1.96 \times 10^{-3}$ M.

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

$$\begin{aligned} \log r &= \log(d[2]/dt) \\ &= \log k + a \log[1] + b \log[\text{SnCl}_2]. \end{aligned} \quad (2)$$

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

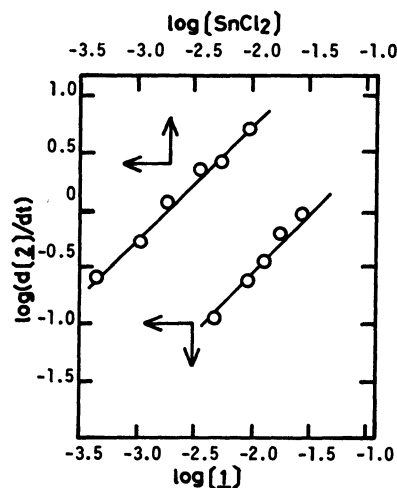
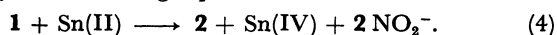


Fig. 3. log-log plots of the initial rate of the reaction of **1** with tin(II) chloride in DMF at 20 °C against the concentrations of **1** and tin(II) chloride.

is kept constant, we may find orders a and b . Plots of both $\log [1]$ and $\log [\text{SnCl}_2]$ vs. $\log r_{t \rightarrow 0}$ 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

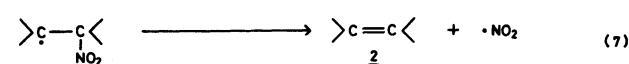
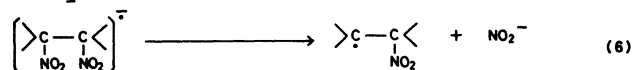
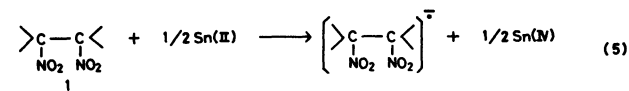
$$r = d[2]/dt = k[1]^{1.00}[\text{SnCl}_2]^{1.04} \quad (3)$$

with a second-order constant $k = 1.49 \times 10^4 \text{ M}^{-1} \text{ min}^{-1}$ ($1 \text{ M} = 1 \text{ mol dm}^{-3}$) at 20 °C. The net reaction is thus given by the following equation:



The mechanism of the present elimination appears to be one of the $\text{E}_{\text{RC}}1^{11}$ 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.

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 $\text{Fe}^{2+} + \text{Co}^{3+} \rightarrow \text{Fe}^{3+} + \text{Co}^{2+}$ 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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