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Kinetics and Mechanism of the Reaction of Iodine with Bis(N, N-di-n-butyldithiocarbamato)zinc(II)

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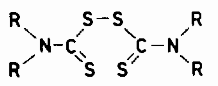
The reaction of bis(N,N-di-n-butyldithiocarbamato)zinc(II), $Zn(n\text{-}Bu_2dtc)_2$, with iodine in cyclohexane was studied employing a stopped-flow technique under pseudo-first-order conditions with excess $Zn(n\text{-}Bu_2dtc)_2$. The rate data indicate that the reaction proceeds via the formation of a charge-transfer complex $Zn(n\text{-}Bu_2dtc)_2 \cdot I_2$, and obeys second-order kinetics for the concentration of $Zn(n\text{-}Bu_2dtc)_2$. These results are interpreted by a mechanism that involves a bimolecular reaction between the charge-transfer complex and the parent $Zn(n\text{-}Bu_2dtc)_2$ compound. The thermodynamic parameters for the formation of the charge-transfer complex were determined ($K = 1.47 \times 10^2\ M^{-1}$, $\Delta H^\circ = -30.2$ kJ mol^{-1}, $\Delta S^\circ = -59.4$ J mol^{-1} deg^{-1} at 25 °C) and the transition state in the bimolecular pathway is proposed.

Introduction

A number of reactions of dithiocarbamato metal complexes with halogens have been studied [1–17]. They are classified into the following two types [18]; (i) the oxidation of the dithiocarbamato ligand by halogen into thiuramdisulfide (1) or dipositive trithiolane (2) which is an oxidation product of 1 by halogen, and (ii) the oxidative addition reaction of halogen to the metal center of dithiocarbamato complexes. The kinetics of these reactions, however, have been little studied.



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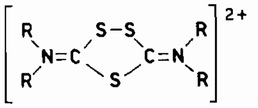

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Our recent kinetic study [15] has shown that the reaction of bis(N,N-diethyldithiocarbamato)dimethyltin(IV), $Me_2Sn(Et_2dtc)_2$, with iodine (type i) could best be described in terms of a mechanism involving a charge-transfer complex, formed by an electrophilic attack of I_2 on the sulfur atom of the dithiocarbamato ligand, followed by decomposition in the rate-determining step to afford N,N-diethyldithiocarbamatoiododimethyltin(IV), $Me_2SnI(Et_2dtc)$, and **1**. It is of interest to examine whether this mechanism is general in the reaction of the type (i), and to determine the role of the charge-transfer complex in the reaction.

This paper reports the kinetic study of the reaction between bis(N,N-di-n-butyldithiocarbamato)zinc (II) and iodine. This reaction was already reported to give diiodo-N,N,N′,N′-tetra-n-butylthiuramdisulfide-zinc(II), $ZnI_2(n\text{-}Bu_4tds)$ (tds = >NC(S)S$_2$C(S)N<), by Brinkhoff, *et al.* [4].

Experimental

Materials

$Zn(n\text{-}Bu_2dtc)_2$ was prepared according to the literature method [19], and recrystallized from ligroin; mp 107 °C (ref. 107.3 °C). *Anal.* Found: C, 45.43; H, 7.85; N, 5.88%. Calcd for $C_{18}H_{36}N_2S_4Zn$: C, 45.60; H, 7.65; N, 5.91%. Iodine and cyclohexane used as the solvent were purified as described previously [15].

Stoichiometry

A solution of I_2 (0.50 mmol) in cyclohexane (20 ml) was added to $Zn(n\text{-}Bu_2dtc)_2$ (1.50 mmol) in the same solvent (20 ml) at room temperature. The iodine color disappeared immediately. The solution was stirred for 10 min. The resulting precipitate was filtered and recrystallized from a carbon disulfide/petroleum ether mixture to afford $ZnI_2(n\text{-}Bu_4tds)$ (0.45 mmol); mp 152 °C. *Anal.* Found: C, 29.75; H, 5.08; N, 3.93%. Calcd for $C_{18}H_{36}N_2S_4I_2Zn$: C, 29.70; H, 4.99; N, 3.85%.

The stoichiometry of the reaction of I_2 with excess $Zn(n\text{-}Bu_2dtc)_2$ is, therefore, expressed as follows;

$$Zn(n\text{-}Bu_2dtc)_2 + I_2 \longrightarrow ZnI_2(n\text{-}Bu_4tds) \qquad (1)$$

Spectra

Electronic spectra were recorded on a Hitachi 124 spectrophotometer. Rapid scanning spectra were measured on a Union RA-1300 stopped-flow spectrophotometer.

Kinetic Measurements

Kinetic runs were carried out under pseudo-first-order conditions with at least a 20-fold excess of $Zn(n\text{-}Bu_2dtc)_2$. The reaction rate was followed by measuring the absorbance of the reaction mixture, using a Union RA-1100 stopped-flow spectrophotometer equipped with a thermostated cell holder. The temperature was maintained constant to within ±0.1 °C.

The decay of absorbance with time was monitored on a Hitachi V-108 memoriscope. For each run at least four traces were superimposed before taking the photograph. Pseudo-first-order rate constants were obtained from the plots of $\ln(A_t - A_\infty)$ against time, where A_t and A_∞ are absorbances at a given wavelength at time t and at the end of the reaction, respectively. The plots were linear to 80% completion. Rate constants were calculated by the use of a linear least-squares program.

Results and Discussion

Rapid scanning spectra of the solution just after mixing of I_2 with excess $Zn(n\text{-}Bu_2dtc)_2$ in cyclohexane are illustrated in Figure 1, which shows a decay of absorbances at 355 and 480 nm both with a half-life of about 50 msec. This result is similar to that obtained in the reaction of $Me_2Sn(Et_2dtc)_2$ with I_2 [15]. Iodine, $Zn(n\text{-}Bu_2dtc)_2$ and $ZnI_2(n\text{-}Bu_4tds)$ do not show any absorption in these regions. The 355 nm band is, therefore, assigned to the charge transfer transition from the sulfur atom of the dithiocarbamato ligand to I_2 and the 480 nm absorption to the blue-shift band of I_2, as discussed in the previous paper [15]. Thus, the CT complex (**3**) formed during the period of mixing would be an intermediate in the reaction.

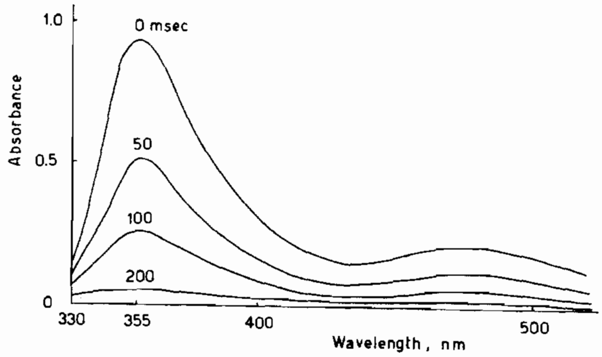
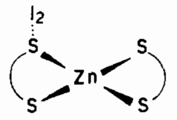


Figure 1. The decay of the electronic spectrum after mixing I_2 (3.00×10^{-4} *M*) with excess $Zn(n\text{-}Bu_2dtc)_2$ (1.00×10^{-2} *M*) in cyclohexane; scanning speed = 150 nm/5 msec, cell length = 1.0 cm.



3 S⌒S = $S_2CN(n\text{-}Bu)_2$

The rate of reaction was followed by monitoring the decay of absorbances at 360 and 500 nm. Pseudo-first-order rate constants, k_{obsd}, were evaluated from the slopes of the $\ln(A_t - A_\infty)$ *vs.* time plots at various concentrations of $Zn(n\text{-}Bu_2dtc)_2$. The results are listed in Table I.

TABLE I. Observed Rate Constants for the Reaction of I_2 with Excess $Zn(n\text{-}Bu_2dtc)_2$ in Cyclohexane.

Temp (°C)	$10^4[I_2]$ (*M*)	$10^3[Zn(n\text{-}Bu_2dtc)_2]$ (*M*)	k_{obsd} (sec^{-1})	
			360 nm	500 nm
15.0	2.03	6.05	8.53	8.98
		8.02	11.8	11.4
		10.0	16.5	17.3
		12.0	20.9	22.6
		16.0	30.5	32.1
25.0	1.00	2.04	1.63	1.89
		3.01	3.22	3.57
		4.02	4.82	5.21
		5.01	7.73	7.94
		6.00	10.4	10.5
		8.02	15.9	16.1
		10.0	20.6	
		12.0	25.7	
	1.47	3.01	3.04	
		4.50	5.53	
		6.00	8.52	
		7.57	13.8	
		9.00	17.3	
		12.0	23.4	
		15.1	34.6	
	2.02	4.04	4.85	6.12
		8.03	11.6	15.5
		12.0	25.0	25.9
		16.0	35.7	40.5
		20.0	48.7	52.2
35.0	2.03	6.02	10.1	10.8
		8.00	15.5	17.6
		10.0	21.7	24.9
		12.0	27.2	30.6
		16.0	42.6	

The fairly good agreement between the k_{obsd} values at 360 and 500 nm supports the assignment of the absorption bands described above.

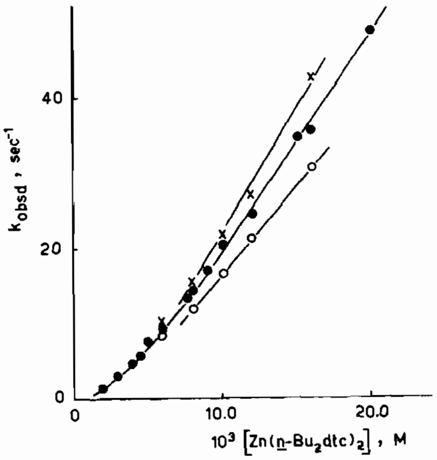


Figure 2. Plots of k_{obsd} (300 nm) against $[Zn(n\text{-}Bu_2dtc)_2]$; ○ 15 °C, ● 25 °C, and × 35 °C.

The plots of k_{obsd} against the $Zn(n\text{-}Bu_2dtc)_2$ concentration are shown in Figure 2. There can be seen a linear relationship at high concentrations of $Zn(n\text{-}Bu_2dtc)_2$. Thus, k_{obsd} is expressed as follows;

$$k_{obsd} = k[Zn(n\text{-}Bu_2dtc)_2] \qquad (2)$$

where k is the rate constant of reaction at a fixed concentration of I_2. At lower concentrations of $Zn(n\text{-}Bu_2dtc)_2$, however, the plots deviate from the straight line. This behavior suggests that the reaction rate may be contributed by higher-order terms of the $Zn(n\text{-}Bu_2dtc)_2$ concentration. The data were analysed graphically in various manners. As a result, the plots of $[Zn(n\text{-}Bu_2dtc)_2]/k_{obsd}$ against $1/[Zn(n\text{-}Bu_2dtc)_2]$ gave a straight line over the observed range of excess $Zn(n\text{-}Bu_2dtc)_2$ concentrations, as depicted in Figure 3. This result suggests the following pathway, (3) and (4):

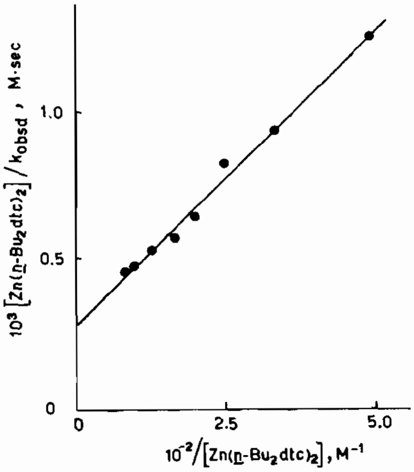


Figure 3. Plots of $[Zn(n\text{-}Bu_2dtc)_2]/k_{obsd}$ against $1/[Zn(n\text{-}Bu_2dtc)_2]$ for the reaction of I_2 with excess $Zn(n\text{-}Bu_2dtc)_2$ at 25 °C; $[I_2] = 1.0 \times 10^{-4}$ M.

$$Zn(n\text{-}Bu_2dtc)_2 + I_2 \overset{K}{\rightleftharpoons} \underset{\mathbf{3}}{Zn(n\text{-}Bu_2dtc)_2{\cdot}I_2} \qquad (3)$$

$$\mathbf{3} + Zn(n\text{-}Bu_2dtc)_2 \xrightarrow{k} Zn(n\text{-}Bu_2dtc)_2 + ZnI_2(n\text{-}Bu_4tds) \qquad (4)$$

The equation (3) corresponds to the rapid formation of the 1:1 charge-transfer complex of I_2 with $Zn(n\text{-}Bu_2dtc)_2$, which can react with additional $Zn(n\text{-}Bu_2dtc)_2$ by a bimolecular manner (Eq. 4).

According to this reaction pathway, k_{obsd} is expressed by Eq. (5):

$$k_{obsd} = \frac{kK[Zn(n\text{-}Bu_2dtc)_2]^2}{1 + K[Zn(n\text{-}Bu_2dtc)_2]} \qquad (5)$$

It is evident that the limiting expression (2) at high concentrations of $Zn(n\text{-}Bu_2dtc)_2$ is readily derived from (5). A transformation of (5) gives (6),

$$\frac{[Zn(n\text{-}Bu_2dtc)_2]}{k_{obsd}} = \frac{1}{kK}\,\frac{1}{[Zn(n\text{-}Bu_2dtc)_2]} + \frac{1}{k} \qquad (6)$$

which is consistent with the observed rate profile (Figure 3). Thus, k and K were obtained from plots of $[Zn(n\text{-}Bu_2dtc)_2]/k_{obsd}$ against $1/[Zn(n\text{-}Bu_2dtc)_2]$, with intercept 1/k and slope 1/kK. The results are given in Table II.

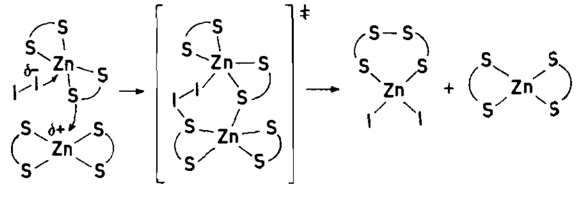
TABLE II. Equilibrium Constants and Reaction Rates for the System I_2–Excess $Zn(n\text{-}Bu_2dtc)_2$ in Cyclohexane.

Temp (°C)	10^4 [I_2] (*M*)	10^{-2} K (M^{-1})	10^{-3} k (M^{-1} sec^{-1}
15.0	2.03	2.38 ± 0.18	2.44 ± 0.08
25.0	1.00	1.53 ± 0.27	3.54 ± 0.43
	1.47	1.47 ± 0.12	3.22 ± 0.21
	2.02	1.42 ± 0.13	3.41 ± 0.18
35.0	2.03	1.07 ± 0.13	4.47 ± 0.50

The K and k values are independent of the initial concentration of iodine within the experimental error. The K value (1.47 × 10^2 M^{-1} at 25 °C) is compared with those of charge-transfer complexes between I_2 and methyl dimethyldithiocarbamate [20], methyl N-methylthiocarbamate [21], or related thiones [20–22].

Thermodynamic parameters of the reactions (3) and (4) were determined from K and k at three different temperatures (Table II). The plot of ln K against 1/T was linear, yielding the values $\Delta H^\circ = -30.2$ kJ mol^{-1} and $\Delta S^\circ = -59.4$ J mol^{-1} deg^{-1} for the reaction (3). The Arrhenius plot of ln k against 1/T also gave the values $E_a = 22.9$ kJ mol^{-1} and $\Delta S^* = -109$ J mol^{-1} deg^{-1} for the reaction (4). It is to be noted that ΔS^* is a large negative value, which is compatible with an associative pathway (Eq. 4).

It would be reasonable to assume that the zinc atom of the CT complex (**3**) is more acidic than that of Zn(n-Bu_2dtc)$_2$, because of the charge transfer from the sulfur atom to I_2 in the former This assumption predicts that the increasing acidity of the zinc atom facilitates the nucleophilic attack of the sulfur atom of the additional Zn(n-Bu_2dtc)$_2$ molecule to afford a transition state (**4**), as shown in the Scheme



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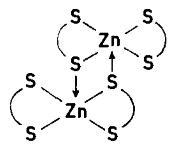
The penta-coordination of Zn(II) is well known in solid Zn(Et_2dtc)$_2$ which exists as a dimer (**5**) [23], while it is monomeric in cyclohexane [24] Although there is no direct evidence for the actual structure of the transition state, an analogous bimolecular mechanism was suggested by Fackler, *et al* for the ligand exchange between bis(dithiocumato)zinc(II) and its trithiocumato analog [25]



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