The Kinetics and Mechanisms of Reaction of Iodine with Bis(*N*,*N*-diethyldithiocarbamato)dimethyltin(IV) and Related Compounds

Hidetoshi Kita, Koji Tanaka, and Toshio Tanaka

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

(Received March 25, 1975)

The reactions of $Me_2SnL(S_2CNEt_2)$ ($L=S_2CNEt_2$ (**1**) and I (**2**)) with iodine in cyclohexane were investigated employing a stopped-flow technique. The kinetic data indicate that the reaction in the presence of a large excess of **1** or **2** proceeds *via* a charge-transfer complex of $Me_2SnL(S_2CNEt_2)\cdot I_2$, which decomposes in the rate-determining step to yield $Me_2SnI(L)$ and unstable $I(S_2CNEt_2)$. This unstable intermediate reacts with the excess **1** or **2** to afford $Me_2SnI(L)$ and tetraethylthiuramdisulfide (**3**). The reaction of **1** with a large excess of I_2 was also kinetically studied to reveal the formation of the 1 : 2 complex, $Me_2Sn(S_2CNEt_2)_2\cdot 2I_2$, as an intermediate; this intermediate then undergoes a simultaneous degradation to afford Me_2SnI_2 and **3**. The transition state in the reaction is discussed.

Several reactions of dithiocarbamato-metal complexes with halogen have been reported thus far; bis(*N*,*N*-dialkyldithiocarbamato)zinc(II), -cadmium(II) and -mercury(II) react with X_2 (X=Cl, Br, I) in the mole ratio of 1 : 1 to give adducts between MX_2 (M=Zn, Cd, Hg) and tetraalkylthiuramdisulfide, $MX_2(R_4tds)$ ($R_4tds=[R_2NC(S)S\text{-}]_2$).[1] On the other hand, *N*,*N*-dialkyldithiocarbamato complexes of Cu(I),[2] Au(I)[2] and Ni(II)[1] oxidatively add X_2 to yield $MX_2(S_2CNR_2)$ (M=Cu, Au) and $NiX(S_2CNR_2)_3$ respectively. These reactions, however, have not been studied kinetically.

Recently, we have noticed that $Me_2Sn(S_2CNEt_2)_2$ and $Me_2SnI(S_2CNEt_2)$ react with I_2 to give $Me_2SnI(S_2CNEt_2)$ and Me_2SnI_2 respectively, together with tetraethylthiuramdisulfide. This paper will report on our kinetic and mechanistic studies of these reactions as well as that of $Me_2Sn(S_2CNEt_2)_2$ with an excess of I_2 in cyclohexane. The stability constant of the charge-transfer complex between tetraethylthiuramdisulfide and iodine is also obtained.

Experimental

Materials. Bis(*N*,*N*-diethyldithiocarbamato)dimethyltin(IV), $Me_2Sn(dtc)_2$ ($dtc=S_2CNEt_2$), was obtained as has been described in a previous paper.[3] *N*,*N*-Diethyldithiocarbamatodimethyliodotin(IV), $Me_2SnI(dtc)$, was prepared by the reaction of $Me_2SnCl(dtc)$ with a large excess of NaI in acetone in the manner described previously;[3] it was then recrystallized from ligroin; mp 124 °C. Found: C, 19.82; H, 4.04; N, 3.50%. Calcd for $C_7H_{16}NS_2ISn$: C, 19.84; H, 3.81; N, 3.31%.

Iodine was purified by sublimation five times. Commercially available tetraethylthiuramdisulfide, Et_4tds (tds=$\rangle$NC(S)S·SC(S)N$\langle$), was recrystallized from ligroin; mp 70 °C. Cyclohexane used as a solvent in the kinetic experiments was purified in the usual manner.[4]

Reactions. (i) A solution of I_2 (1.02 mmol) in benzene (20 ml) was added to $Me_2Sn(dtc)_2$ (2.38 mmol) in the same solvent (20 ml) at room temperature. The solution was stirred for 30 min, and then evaporated to dryness under reduced pressure. The resulting solid was recrystallized from ligroin to afford white crystals of $Me_2SnI(dtc)$ (1.87 mmol). The filtrate after recrystallization was evaporated to dryness again to give Et_4tds (0.84 mmol).

(ii) A benzene solution (20 ml) containing I_2 (0.5 mmol) and $Me_2SnI(dtc)$ (1.9 mmol) was stirred for 1 hr at room temperature; the subsequent application of the procedure described above gave Me_2SnI_2 (0.6 mmol).

(iii) A benzene solution (20 ml) of $Me_2Sn(dtc)_2$ (2.3 mmol) was added to the excess of I_2 (4.5 mmol) in the same solvent (20 ml) at room temperature. The solution was then stirred for 3.5 hr, filtered, and evaporated to a small volume. The precipitate which appeared was collected by filtration and recrystallized from petroleum ether to afford $Me_2SnI(dtc)$ (0.3 mmol). The filtrate was evaporated to give a solid product, from which Me_2SnI_2 (1.5 mmol) was obtained.

Spectra. The electronic spectra were recorded on a Hitachi 124 spectrophotometer. The infrared spectra were measured in Nujol mulls on a Hitachi EPI-L spectrophotometer.

Kinetics. Kinetic experiments were carried out under pseudo-first-order conditions at 25 °C, using at least a tenfold excess amount of either iodine or the tin compound. The rate of reaction was followed by monitoring the transmittance at a fixed wavelength in the electronic spectra of the reaction mixture, using a Union RA-1100 stopped-flow spectrophotometer equipped with a 1-cm quartz cell. The measurements were usually made over a period of 3 half-lives of the reaction. Pseudo-first-order rate constants, k_{obsd}, were obtained from the semi-logarithmic 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. Rapid scanning spectra were measured on a Union RA-1300 stopped-flow reaction analyzer in order to determine the wavelength of which the reaction could best be followed.

Results and Discussion

Stoichiometry of the Reaction. The reaction of I_2 with excess $Me_2Sn(dtc)_2$ rapidly proceeds to give $Me_2SnI(dtc)$ and Et_4tds in good yields. Iodine also reacts with $Me_2SnI(dtc)$ to afford Me_2SnI_2 and Et_4tds; this reaction is reversible. The forward and backward reactions require a few minutes and several days respectively to come to an equilibrium. Thus, the stoichiometry for the reaction of $Me_2Sn(dtc)_2$ with I_2 may be expressed as follows:

$$Me_2Sn(dtc)_2 + \frac{1}{2}I_2 \xrightarrow{\text{fast}} Me_2SnI(dtc) + \frac{1}{2}Et_4tds \quad (1)$$

$$Me_2SnI(dtc) + \frac{1}{2}I_2 \underset{\text{very slow}}{\overset{\text{slow}}{\rightleftarrows}} Me_2SnI_2 + \frac{1}{2}Et_4tds \quad (2)$$

Stability Constant of the Charge-transfer Complex between I_2 and Et_4tds. By analogy with the formation of a stable charge-transfer complex between I_2 and

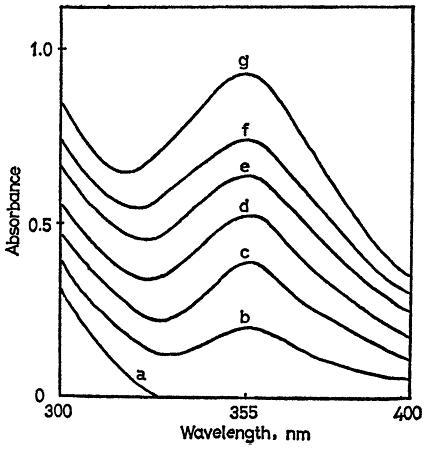


Fig. 1. Absorption spectra of Et_4tds in cyclohexane (1.0×10^{-4} M) containing varying amounts of I_2: (a) 0, (b) 1.0×10^{-3}, (c) 2.0×10^{-3}, (d) 3.0×10^{-3}, (e) 4.0×10^{-3}, (f) 5.0×10^{-3}, (g) 8.0×10^{-3} M (25 °C).

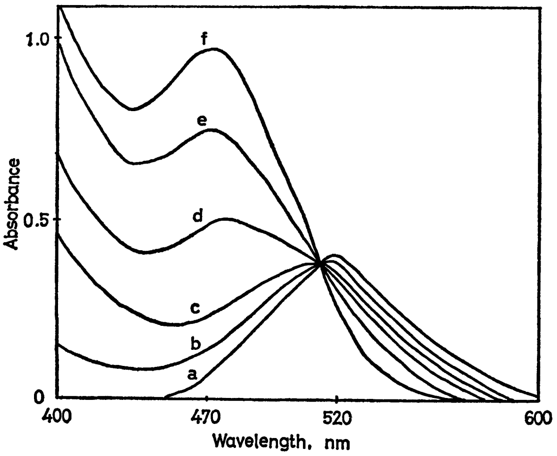


Fig. 2. Absorption spectra of I_2 in cyclohexane (8.0×10^{-4} M) containing varying amounts of Et_4tds: (a) 0, (b) 8.0×10^{-4}, (c) 1.6×10^{-3}, (d) 4.0×10^{-3}, (e) 8.0×10^{-3}, (f) 1.6×10^{-2} M (25 °C).

N-methylthioacetamide,[5] *N*-methylthiocarbamate[5] or other sulfur containing compounds,[5,6] I_2 may be expected to form a complex with Et_4tds, which is the reaction product between I_2 and $Me_2Sn(dtc)_2$ or $Me_2SnI(dtc)$. In accordance with this, cyclohexane solutions containing Et_4tds and I_2 exhibit an absorption at 355 nm, which is intensified with an increase in the amounts of I_2, as is shown in Fig. 1. Thus, the 355 nm band can unequivocally be assigned to the CT transition from Et_4tds to I_2. Figure 2 shows the electronic spectra of I_2 in cyclohexane containing varying amounts of Et_4tds. The 520 nm band due to I_2 is shifted to a short wavelength (470 nm) by adding Et_4tds, and an isosbestic point is observed at 515 nm. The continuous-variation method at 470 nm revealed that the composition of the CT complex is 1 : 1. Thus, the following equilibrium takes place in solution:

$$I_2 + Et_4tds \rightleftharpoons I_2\cdot Et_4tds \tag{3}$$

The equilibrium constant, as calculated from the absorbances at 470 nm ($\varepsilon_{max}=2.14\times10^3$) by means of the Rose-Drago equation,[7] was $K=3.75\ (\pm0.01)\times10^2$ in cyclohexane at 25 °C.

Reaction of I_2 with Excess $Me_2Sn(dtc)_2$ or $Me_2SnI(dtc)$. The rapid scanning spectra for the reaction of I_2 with excess $Me_2Sn(dtc)_2$ are depicted in Fig. 3, which reveals that a strong band appears at 386 nm immediately after mixing and that the band decays with a half-life of about 200 ms. An almost identical half-life of decay was found at the 520 nm band. The reaction of I_2 with excess $Me_2SnI(dtc)$ also showed the decay of the 386 nm band with a half-life of about 40 s. However, the CT band due to $I_2\cdot Et_4tds$ at 355 nm was not observed at all.

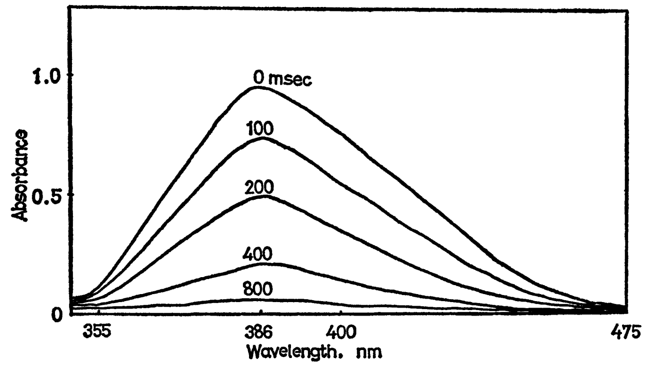


Fig. 3. The decay of the electronic spectrum after mixing I_2 (1.7×10^{-3} M) with $Me_2Sn(dtc)_2$ (3.0×10^{-2} M) in cyclohexane at 25 °C.

The rate of reaction was followed by measuring the transmittances at 386 and 520 nm of a solution right after the mixing of I_2 with excess $Me_2Sn(dtc)_2$. The Guggenheim plots showed a good linear relationship between $\ln(A_t-A_\infty)$ and the time. Thus, the reaction apparently obeys the first-order kinetics with respect to I_2. The apparent first-order rate constants, k_{obsd}, obtained at various concentrations of $Me_2Sn(dtc)_2$ are collected in Table 1.

Plots of the rate constants obtained from the decay of the transmittances at 386 and 520 nm against the concentration of $Me_2Sn(dtc)_2$ showed a good linearity, as may be seen in Fig. 4; this indicates that the reaction is first-order in both I_2 and $Me_2Sn(dtc)_2$.

Taking into account this result and the fact that I_2 can form CT complexes with various sulfur-containing compounds,[5,6] the band at 386 nm may be

TABLE 1. APPARENT RATE CONSTANTS FOR THE REACTIONS OF $Me_2Sn(dtc)_2$ WITH I_2 AT VARIOUS MOLE RATIOS IN CYCLOHEXANE AT 25 °C. $[I_2]=3.0\times10^{-4}$ M

$[Sn]/[I_2]$	10	20	30	40	50	60	80
k_{obsd} (386 nm)	0.263	0.527	0.846	1.08	1.32	1.57	2.24
k_{obsd} (520 nm)	0.268	0.555	0.761	1.02	1.32	1.63	2.16

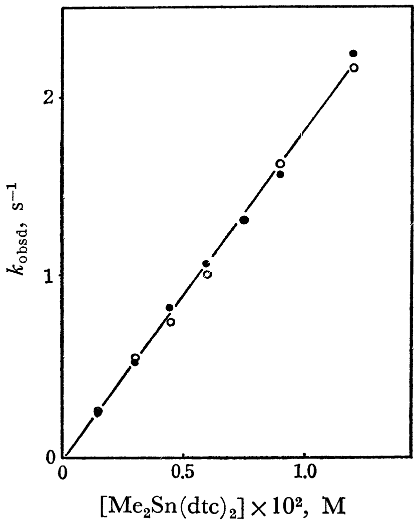


Fig. 4. Plots of the apparent rate constant against the $Me_2Sn(dtc)_2$ concentrations; ● 386 nm, ○ 520 nm.

assigned to the CT complex formed between I_2 and $Me_2Sn(dtc)_2$ in the initial process. The addition of Et_4tds to the reactant solution caused no appreciable decrease in the rate of reaction. Thus, the following pathways for the reaction may reasonably be suggested:

$$Me_2Sn(dtc)_2 + I_2 \overset{K_1}{\rightleftharpoons} Me_2Sn(dtc)_2 \cdot I_2 \quad (4)$$

$$Me_2Sn(dtc)_2 \cdot I_2 \xrightarrow{k_1} Me_2SnI(dtc) + I(dtc) \quad (5)$$

$$I(dtc) + Me_2Sn(dtc)_2 \xrightarrow{\text{fast}} Me_2SnI(dtc) + Et_4tds \quad (6)$$

Reaction (5) represents the rate-determining step, producing unstable I(dtc). Although there is no evidence for the formation of I(dtc) as an intermediate, a somewhat analogous species, ISCN, has been reported to exist in the following equilibrium:[8]

$$I^- + (SCN)_2 \rightleftharpoons I(SCN)_2^- \rightleftharpoons ISCN + SCN^- \quad (7)$$

It may be possible that the two molecules of I(dtc) produced in Eq. (5) react with each other to afford I_2 and Et_4tds, but this reaction dose not seem to occur, since no band was observed at 355 nm (due to $I_2 \cdot Et_4tds$) at all in the presence of excess $Me_2Sn(dtc)_2$. Instead, I(dtc) must react rapidly with excess $Me_2Sn(dtc)_2$ to give $Me_2SnI(dtc)$ and Et_4tds, as is shown in Eq. (6). According to this reaction scheme, k_{obsd} can be expressed by Eq. (8):

$$k_{obsd}^{(1)} = \frac{k_1K_1[Me_2Sn(dtc)_2]}{1+K_1[Me_2Sn(dtc)_2]} \quad (8)$$

If $K_1[Me_2Sn(dtc)_2]$ is negligibly small compared with unity, $k_{obsd}^{(1)}$ is reduced to $k_1K_1[Me_2Sn(dtc)_2]$. This expression is consistent with the plots of k_{obsd} against the concentration of $Me_2Sn(dtc)_2$ with a zero intercept (Fig. 4). Thus, k_1K_1 is obtained as $1.84\times10^2\ M^{-1}\,s^{-1}$.

Kinetic experiments on the reaction of $Me_2SnI(dtc)$ with I_2 were carried out by monitoring the transmittance only at 386 nm, since there was no marked change in the transmittance at 520 nm in this system because of the low solubility of $Me_2SnI(dtc)$ in cyclohexane. The k_{obsd} values obtained at various concentrations of $Me_2SnI(dtc)$ are listed in Table 2, which shows the reaction to be first-order in both $Me_2SnI(dtc)$ and I_2.

TABLE 2. APPARENT RATE CONSTANTS FOR THE REACTION OF $Me_2SnI(dtc)$ WITH I_2 AT VARIOUS MOLE RATIOS IN CYCLOHEXANE AT 25 °C. $[I_2]=3.3\times10^{-4}$ M

$[Sn]/[I_2]$	23	28	38	47
$k_{obsd}\times10^2$ (386 nm)	1.10	1.24	1.59	2.08

By analogy with the $Me_2Sn(dtc)_2$–I_2 system, the following pathways may be postulated, where $k_2K_2 = 1.37\ M^{-1}\,s^{-1}$:

$$Me_2SnI(dtc) + I_2 \overset{K_2}{\rightleftharpoons} Me_2SnI(dtc) \cdot I_2 \quad (9)$$

$$Me_2SnI(dtc) \cdot I_2 \xrightarrow{k_2} Me_2SnI_2 + I(dtc) \quad (10)$$

$$I(dtc) + Me_2SnI(dtc) \xrightarrow{\text{fast}} Me_2SnI_2 + Et_4tds \quad (11)$$

Since both K_1 and K_2 are unknown, k_1K_1 and k_2K_2 have been difficult to analyze quantitatively.

Reaction of $Me_2Sn(dtc)_2$ with Excess I_2. The rate of reaction was determined from the decay of the transmittance at 386 nm. A good linear relationship between the $\ln(A_t-A_\infty)$* and the time was observed, except for the final short period, in which the 355 nm band arising from the product of $I_2 \cdot Et_4tds$ is intensified and the tail of this band is overlapped with the 386 nm band. Plots of k_{obsd} *vs.* the square of I_2 concentrations gave a straight line in the presence of a large excess of I_2, while a significant deviation from it was observed in the presence of a small excess of I_2, as is shown in Fig. 5. These results may be interpreted by assuming the reaction pathways shown in Scheme 1.

One of the pathways involves the formation of the 1 : 2 adduct between $Me_2Sn(dtc)_2$ and I_2, which

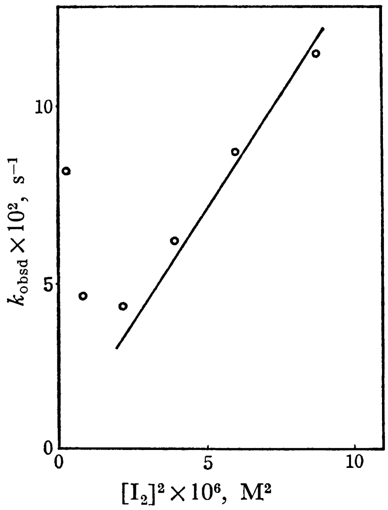
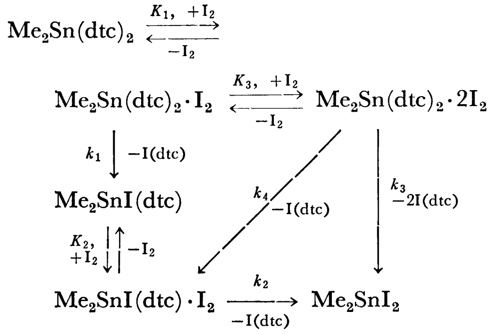


Fig. 5. Plots of the apparent rate constant against the square of the I_2 concentrations; $Me_2Sn(dtc)_2$ 5.1×10^{-4} M.

---

* Here, A_∞ was assumed to be zero.



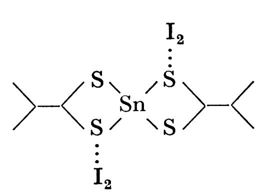
Scheme 1.

undergoes either consecutive (k_4 and k_2 in Scheme 1) or simultaneous (k_3) degradation to yield Me_2SnI_2 and $I_2 \cdot Et_4tds$. These processes can well explain the second-order dependence of the I_2 concentration. Taking into account the result that the reaction is much faster than that of I_2 with excess $Me_2SnI(dtc)$, the simultaneous degradation of the 1 : 2 adduct is preferable to the consecutive one. Another route is the successive formation of two 1 : 1 adducts, $Me_2Sn(dtc)_2 \cdot I_2$ and $Me_2SnI(dtc) \cdot I_2$, followed by degradation such as has been described above. This pathway leads us to the assumption that the reaction obeys the first-order kinetics in the I_2 concentration, because $k_1K_1 \gg k_2K_2$. It may, therefore, be assumed that, in the presence of a small excess of I_2, the processes *via* both the 1 : 1 and 1 : 2 adducts take place. Thus, in the presence of a large excess of I_2, the rate constant can be expressed by Eq. (12):

$$k^{(2)}_{\text{obsd}} = \frac{k_3K_1K_3[I_2]^2}{1+K_1K_3[I_2]^2} \tag{12}$$

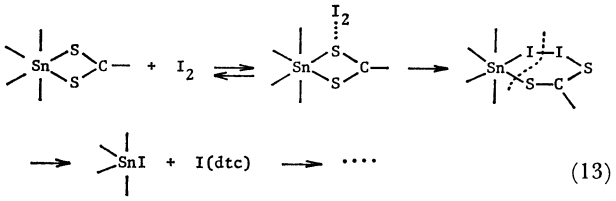
If $K_1K_3[I_2]^2$ is negligibly small compared with unity, one can obtain $k^{(2)}_{\text{obsd}}=k_3K_1K_3[I_2]^2$, which coincides with the experimental data, and $k_3K_1K_3=1.34\times 10^4\ M^{-2}\ s^{-1}$.

There are two possible mechanisms to form the unstable 1 : 2 adduct between $Me_2Sn(dtc)_2$ and I_2. One is a nucleophilic attack of two I_2 molecules on the tin atom. This is, however, not likely to occur, since no eight-coordination of tin is common. The other mechanism is an electrophilic attack of I_2 on the sulfur of separate dithiocarbamato ligands in a given complex, such as is shown in **a**. This can be assumed on the basis of the fact that I_2 forms CT complexes with various sulfur-containing compounds.[5,6]



a

In conclusion, we propose that the reaction proceeds through a transition state involving a six-membered ring formed by the electrophilic attack of I_2 on the sulfur as follows: This mechanism predicts that the stronger Sn–S bond would be, the less reactive toward I_2. This is consistent with the present result that the rate of the reaction of $Me_2SnI(dtc)$ with I_2 is slower than that of $Me_2Sn(dtc)_2$, since the ν(Sn–S) frequency of $Me_2SnI(dtc)$ (393 cm^{-1}) is fairly higher than that of $Me_2Sn(dtc)_2$ (366 cm^{-1}).



(13)

The authors are grateful to the Ministry of Education for a Science Research Grant-in-aid. They are also indebted to Professor Shin-ichi Kawaguchi, Osaka City University, for letting them use the rapid-scan spectrophotometer.

References

1) H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemse, *Rec. Trav. Chim. Pays-Bas*, **88**, 633 (1969).

2) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 272 (1970).

3) M. Honda, M. Komura, Y. Kawasaki, T. Tanaka, and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).

4) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, 2nd Ed., ed. by A. Weissberger, Interscience Publishers, New York, N.Y. (1955), p. 307.

5) K. R. Bhaskar, S. N. Bhat, A. S. N. Murthy, and C. N. R. Rao, *Trans. Faraday Soc.*, **62**, 788 (1966).

6) G. Reichenbach, S. Santini, and U. Mazzucato, *J. Chem. Soc., Faraday I*, **69**, 143 (1973).

7) N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, **81**, 6138 (1959).

8) C. Long and D. A. Skoog, *Inorg. Chem.*, **5**, 206 (1966).