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Kinetics and Mechanism of the Oxidation Reaction of Bis(μ-dibutyldithiocarbamato-*S*,*S*′)-digold(I) by Halogens

Hidetoshi KITA, Kazuyuki ITOH, Koji TANAKA, and Toshio TANAKA*

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

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Kinetics of the reaction of bis(μ-dibutyldithiocarbamato-*S*,*S*′)-digold(I), [Au(*n*-Bu$_2$dtc)]$_2$, with I$_2$, IBr, and Br$_2$ in dichloromethane was studied by the stopped-flow technique. A 1 : 1 charge-transfer (CT) complex, [Au(*n*-Bu$_2$dtc)]$_2$·X$_2$ (X$_2$=I$_2$, IBr, and Br$_2$), formed in the initial process of reaction was identified spectrophotometrically at −50 °C. The rates of reaction were almost the same for I$_2$, IBr, and Br$_2$, and independent of the both [Au(*n*-Bu$_2$dtc)]$_2$ and halogen concentrations. The reaction has been interpreted to proceed *via* the charge-transfer complex, [Au(*n*-Bu$_2$dtc)]$_2$·X$_2$, which decomposes in a rate-determining step to give the final product, [Au$^{\mathrm{III}}$(*n*-Bu$_2$dtc)$_2$][Au$^{\mathrm{I}}$X$_2$]. The activation parameters for the reactions were determined: $\Delta H^{\neq}$(kJ/mol)=43.7 (I$_2$), 26.0 (IBr), and 12.3 (Br$_2$); $\Delta S^{\neq}$(J/(mol K))=−91.5 (I$_2$), −156 (IBr), and −201 (Br$_2$).

Reactions of dithiocarbamato metal complexes with halogens[1–4] are classified into two types; one of them is that the dithiocarbamato ligand is oxidized by halogen to give thiuram disulfide, and the other is the oxidation of the central metal by halogen. The authors previously reported the kinetic studies on the reactions of bis(diethyldithiocarbamato)dimethyltin(IV)[5] and bis(dibutyldithiocarbamato)zinc(II)[6] with iodine in cyclohexane, which belong to the former type of reaction. No kinetic study for the latter type of reaction, however, has been reported so far.

This paper describes a kinetic study on the oxidation reaction of bis(μ-dibutyldithiocarbamato-*S*,*S*′)-digold(I) by iodine, iodine bromide, and bromine in dichloromethane by the stopped-flow method. This reaction is known to give bis(dibutyldithiocarbamato)gold(III) dihalogenoaurate(I).[7,8]

Experimental

Materials. Bis(μ-dibutyldithiocarbamato-*S*,*S*′)-digold(I), [Au(*n*-Bu$_2$dtc)]$_2$ (*n*-Bu$_2$dtc=S$_2$CN(*n*-C$_4$H$_9$)$_2$), was prepared by the literature method[9] and recrystallized twice from 1,2-dichloroethane. Found: C, 26.70; H, 4.52; N, 3.29%. Calcd for $C_{18}H_{36}N_2S_4Au_2$: C, 26.93; H, 4.52; N, 3.49%.

Iodine and iodine bromide were purified by sublimation and bromine by distillation prior to use. A dichloroethane solution of Br$_2$ was standardized by 0.01 N Na$_2$S$_2$O$_3$ containing 0.1 M KI using starch as an indicator before use. Dichloromethane used as a solvent was purified in the usual method.[10]

Reactions of [*Au(*n*-Bu$_2$dtc)*]$_2$ *with Halogens.* A solution of X$_2$ (X$_2$=I$_2$, IBr, and Br$_2$) (0.5 mmol) in CH$_2$Cl$_2$(15 ml) was mixed with [Au(*n*-Bu$_2$dtc)]$_2$ (0.5 mmol) in CH$_2$Cl$_2$(15 ml) at room temperature to give a dark green (I$_2$ and IBr) or a red (Br$_2$) solution, followed by rapid decoloration. The solution was evaporated to dryness under reduced pressure. The resulting solid was recrystallized from acetonitrile to afford yellow needles of [Au$^{\mathrm{III}}$(*n*-Bu$_2$dtc)$_2$][Au$^{\mathrm{I}}$X$_2$] (95% based on the amount of gold). X$_2$=I$_2$: mp 135 °C (lit,[8] 135 °C). Found: C, 20.45; H, 3.44; N, 2.57%. Calcd for $C_{18}H_{36}N_2S_4I_2Au_2$: C, 20.46; H, 3.44; N, 2.65%. X$_2$=IBr: mp 139 °C. Found: C, 21.07; H, 3.49; N, 2.88%. Calcd for $C_{18}H_{36}N_2S_4BrIAu_2$: C, 21.41; H, 3.60; N, 2.78%. X$_2$=Br$_2$: mp 143 °C (lit,[8] 143—144 °C). Found: C, 22.31; H, 3.74; N, 2.91%. Calcd for $C_{18}H_{36}N_2S_4Br_2Au_2$: C, 22.46; H, 3.78; N, 2.91%.

The stoichiometry of reaction of [Au(*n*-Bu$_2$dtc)]$_2$ with halogens is, therefore, expressed as follows:

$$[\mathrm{Au}(n\text{-}\mathrm{Bu_2dtc})]_2 + \mathrm{X_2} \longrightarrow [\mathrm{Au}(n\text{-}\mathrm{Bu_2dtc})_2][\mathrm{AuX_2}].$$

Spectra. Electronic spectra were recorded on a Hitachi 124 (at 25 °C) or a Hitachi 356 (at −50 °C) spectrophotometer, the latter of which was equipped with a glass Dewar. Rapid scanning spectra were measured with a Union RA-1300 stopped-flow rapid scan analyzer.

Kinetic Measurements. Kinetic runs were carried out under the conditions where equimolar amounts of the reactants were used and either one of those was used excessively relative to the other. The rate of reaction was followed by monitoring the absorbance at a fixed wavelength in the electronic spectra of the reaction mixture, using a Union RA-413 stopped-flow spectrophotometer equipped with a 0.2 cm quartz cell in a cell holder thermostated within ±0.2 °C. Absorbance-time data were accumulated at least five times on a Union System-71 data processor and average absorbance-time curves were recorded using a National VP-6421A X-Y recorder. Plots of $\ln|A_t - A_\infty|$ *vs.* time were found to be linear to at least 70% completion, where A_t and A_∞ are absorbances at a given wavelength at a time t and the end of the reaction, respectively. Observed first-order rate constants, k_{obsd}, were obtained by performing the least-squares analysis on the linear region of $\ln|A_t - A_\infty|$ *vs.* time plots.

Results and Discussion

Rapid Scanning Spectra and a Reaction Intermediate. Figure 1 shows a typical example of rapid scanning spectra for the [Au(*n*-Bu$_2$dtc)]$_2$–I$_2$ system. Four absorp-

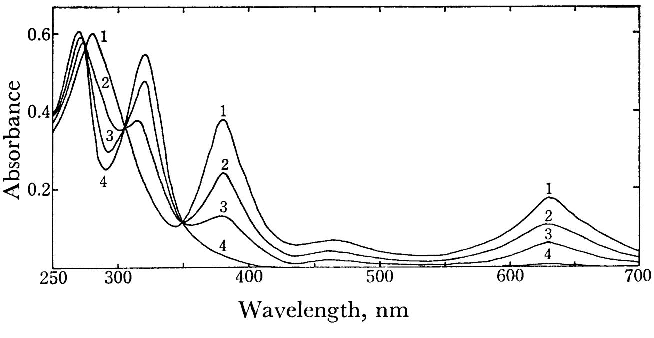


Fig. 1. Rapid scanning spectra of the reaction of [Au(*n*-Bu$_2$dtc)]$_2$ (2.11 × 10^{-4} M) with I$_2$ (2.08 × 10^{-4} M) in CH$_2$Cl$_2$ at 25 °C; scanning speed = 150 nm/5 ms, cell length = 0.2 cm.
1: 0.08 s, 2: 0.48 s, 3: 1.28 s, 4: the end of reaction.

tion peaks at 280, 380, 460, and 630 nm are observed immediately after mixing of the reactants. These bands are weakened with intensifying of the bands newly appeared at 270 and 320 nm, which are assigned to $[Au(n\text{-}Bu_2dtc)_2][AuI_2]$.[8] Then, isosbestic points are found at 275, 305, and 350 nm. This spectral change clearly indicates the occurrence of a transient species as a reaction intermediate. The transient species has been frozen at −50 °C; when a dichloromethane solution of $[Au(n\text{-}Bu_2dtc)]_2$ was mixed with iodine in the same solvent at −50 °C, the solution immediately displayed green color, which did not disappear over 10 h at this temperature, though a decoloration took place almost instantly above −15 °C. The absorption spectrum at −50 °C was quite similar to that immediately after mixing at 25 °C and the green color can be associated with the 630 nm band. It has been reported that $Au^{II}(Et_2dtc)_2$ exhibits an absorption near 600 nm.[11] No ESR signal has, however, been detected for the green solution obtained here, indicating that the transient species is not $Au^{II}(n\text{-}Bu_2dtc)_2$. By analogy with kinetic studies of the $Me_2Sn(Et_2dtc)_2$–I_2[5] and $Zn(n\text{-}Bu_2dtc)_2$–I_2[6] systems, the 380 nm band can be assigned to the charge-transfer (CT) transition from sulfur of the dithiocarbamato ligand to I_2 and the weak absorption at 460 nm to a blue-shifted band of the iodine moiety of the CT complex. The composition of the CT complex was determined by the mole ratio method in the visible spectrum at −50 °C. Figure 2 shows plots of the absorbance at three different wavelengths against the mole ratio of I_2 to the gold(I) complex, indicating the composition of 1 : 1. It is to be noted that the band characteristic of $[Au(n\text{-}Bu_2dtc)]_2$ underwent only a little shift upon CT complexation (287→280 nm). This fact indicates that the CT complex may retain the parent dimeric structure of $[Au(n\text{-}Bu_2dtc)]_2$. The gold-gold distance in $[Au(n\text{-}Pr_2dtc)]_2$ was reported to be shorter than that in metallic gold,[12] however the valence state of Au(I), $5d^{10}$, predicts the presence of no metal-metal bondings. In spite of this, the fact that $[Au(n\text{-}Bu_2dtc)]_2\cdot I_2$ exhibited the absorption band at 630 nm suggests the CT complex involving the skeleton with a gold-gold interaction shown in **1**. The Au(I)–Au(I) interaction would account for the absorption band at 630 nm observed in the CT complex.

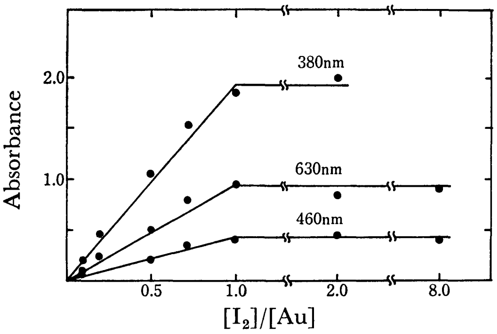
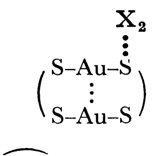


Fig. 2. Mole ratio study of $[Au(n\text{-}Bu_2dtc)]_2$–I_2 system in CH_2Cl_2 at −50 °C; $[Au(n\text{-}Bu_2dtc)]_2=5.0\times10^{-5}$ M.



1: S⌒S $=S_2CN(n\text{-}Bu)_2$.

The $[Au(n\text{-}Bu_2dtc)]_2$–IBr and –Br_2 systems also exhibited absorption maxima due to the CT transition at 380 nm. No blue-shifted band of halogens has, however, been observed in these systems (Table 1). This is probably due to the masking of it by the tail of the intense CT band at 380 nm, because of small molar extinction coefficients of IBr and Br_2 compared with that of I_2; $\varepsilon_{486nm}=3.7\times10^2$, $\varepsilon_{406nm}=2.6\times10^2$, and $\varepsilon_{505nm}=9.0\times10^2$ M^{-1} cm^{-1} for IBr, Br_2, and I_2 in CH_2Cl_2, respectively.

Table 1. Electronic spectra of $[Au(n\text{-}Bu_2dtc)]_2$, $[Au(n\text{-}Bu_2dtc)]_2\cdot X_2$, and $[Au(n\text{-}Bu_2dtc)_2]$-$[AuX_2]$ in CH_2Cl_2 at 25 °C

	λ_{max} / nm	ε[a)] / $M^{-1}cm^{-1}$
$[Au(n\text{-}Bu_2dtc)]_2$	287	4.0×10^4
$[Au(n\text{-}Bu_2dtc)]_2\cdot X_2$		
$X_2=I_2$	280	b)
	380	(3.9×10^4)
	460	(8.3×10^3)[c)]
	630	(1.8×10^4)
IBr	280	b)
	380	
	600	
Br_2	280	
	380	
	560	
$[Au(n\text{-}Bu_2dtc)_2][AuX_2]$		
$X_2=I_2$	270	4.0×10^4
	320	3.9×10^4
IBr	270	3.5×10^4
	320	3.0×10^4
Br_2	270	3.8×10^4
	320	3.1×10^4

a) Values in parentheses were calculated from the visible spectrum at −50 °C. b) Not measured. c) Uncorrected for the contribution from the overlap with the CT band.

Molar extinction coefficients of the absorptions arising from the CT complex were determined from the visible spectra of dichloromethane solutions containing a fixed amount of the gold(I) complex and large excess I_2 or *vice versa* at −50 °C. The result is listed in Table 1 together with the ε values of absorptions due to $[Au(n\text{-}Bu_2dtc)]_2$ and $[Au(n\text{-}Bu_2dtc)_2][AuX_2]$. The ε value of the 380 nm band is very close to those of CT bands of the I_2 complexes with methyl dimethyldithiocarbamate ($\varepsilon_{347nm}=3.0\times10^4$ M^{-1} cm^{-1}) and tetraethylthiuram disulfide ($\varepsilon_{356nm}=3.8\times10^4$ M^{-1} cm^{-1}).[13] On the other hand, the value of the blue-shifted band of iodine (460 nm) is larger than those of other known iodine complexes ($\varepsilon_{max}=(2.7$—$4.2)\times10^3$ M^{-1} cm^{-1}).[13–17] This is due to an overlapping of this band with the tail of the CT band.

TABLE 2. OBSERVED RATE CONSTANTS FOR THE REACTION OF $[Au(n\text{-}Bu_2dtc)]_2$ WITH I_2 IN CH_2Cl_2 AT 25 °C

$\frac{I_2}{M}$	$\frac{[Au(n\text{-}Bu_2dtc)]_2}{M}$	$\frac{k_{obsd}}{s^{-1}}$			
		630 nm	460 nm	380 nm	320 nm
1.04×10^{-4}	1.06×10^{-4}	2.70		2.04	
1.04×10^{-3}		2.43		2.06	
2.08×10^{-3}		2.60		2.44	
2.08×10^{-4}	2.11×10^{-4}	2.51		2.23	2.90
4.93×10^{-4}	5.03×10^{-4}	2.65	2.65	2.11	2.87
3.91×10^{-3}		2.46			
9.46×10^{-5}	2.00×10^{-4}	2.50		2.68	
	2.00×10^{-5}	2.36		2.23	
1.02×10^{-4}	1.00×10^{-3}	2.35	2.00	2.05	
	2.04×10^{-3}	2.35	2.00	2.17	
	3.03×10^{-3}	2.40	2.28	2.38	
	3.96×10^{-3}	2.06	2.14	2.29	
	4.98×10^{-3}	2.39	2.25	2.10	
		Average = 2.35 ± 0.24[a]			

a) A standard deviation.

Kinetics and Mechanism. The rate of reaction was determined by following the decomposition of $[Au(n\text{-}Bu_2dtc)]_2\cdot X_2$ and the formation of $[Au(n\text{-}Bu_2dtc)_2][AuX_2]$. Observed first-order rate constants, k_{obsd}, obtained from the decay of three band maxima of the CT complex and the rise of a band maximum of the product for the reaction of $[Au(n\text{-}Bu_2dtc)]_2$ with I_2 in CH_2Cl_2 at 25 °C are listed in Table 2, which indicates that the k_{obsd} values obtained from the different wavelengths are consistent with one another within experimental error. They are also essentially the same in various concentrations and varying mole ratios of the reactants, indicating that the reaction is independent of both concentrations of $[Au(n\text{-}Bu_2dtc)]_2$ and I_2 in the measured range. Similar kinetic results were obtained in the $[Au(n\text{-}Bu_2dtc)]_2$–IBr and –Br_2 systems. It is therefore suggested that the reaction of $[Au(n\text{-}Bu_2dtc)]_2$ with halogens proceeds *via* a CT complex, which decomposes to give the final product as follows:

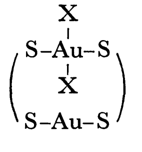
$$\begin{tikzcd}[Au(n\text{-}Bu_2dtc)]_2 + X_2 \arrow[r, "\text{fast}"] & {[Au(n\text{-}Bu_2dtc)]_2\cdot X_2} \arrow[d, "k"] \\ & {[Au(n\text{-}Bu_2dtc)_2][AuX_2],}\end{tikzcd}$$

where k is equal to k_{obsd}. According to this scheme, the rate law can be written as

$$\frac{d[[Au(n\text{-}Bu_2dtc)_2][AuX_2]]}{dt} = -\frac{d[[Au(n\text{-}Bu_2dtc)]_2\cdot X_2]}{dt} = k[[Au(n\text{-}Bu_2dtc)]_2\cdot X_2].$$

Rate constants and activation parameters obtained from the Eyring plots of $\ln(k/T)$ against $1/T$ are summarized in Table 3.

Although there is no direct evidence for another transient species, at least two possible intermediates,



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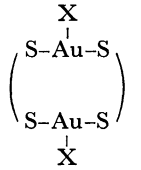

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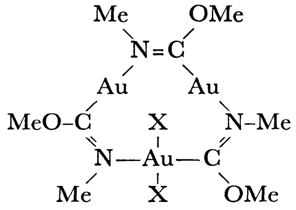
2 and **3**, can be envisaged in the decomposition pathway. Intermediate **2** which is a mixed valence gold(III)–gold(I) complex may be formed by the attack of iodine at a single gold atom. Alternatively, the simultaneous attack of iodine at both gold atoms will afford the gold(II) complex, **3**. The existence of both **2** and **3** may be supported from the fact that analogous gold complexes, **4** and **5**, were isolated in the oxidation



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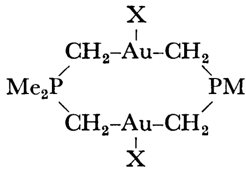

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reactions of trimeric[18] and dimeric[19] gold(I) complexes with halogen, respectively. Of the two possible inter-

TABLE 3. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTION OF $[Au(n\text{-}Bu_2dtc)]_2$ WITH X_2 IN CH_2Cl_2[a]

X_2	$\frac{\text{Temp}}{°C}$	No. of runs	$\frac{k}{s^{-1}}$	$\frac{\Delta H^{\ddagger}}{kJ\,mol^{-1}}$	$\frac{\Delta S^{\ddagger}}{J\,mol^{-1}K^{-1}}$
I_2	10.1	15	0.89 ± 0.09	43.7 ± 8.4	-91.5 ± 28.9
	15.5	15	1.23 ± 0.10		
	20.2	34	1.75 ± 0.10		
	25.0	33	2.35 ± 0.24		
IBr	11.1	8	0.68 ± 0.13	26.0 ± 16.1	$-156\ \pm55$
	15.3	12	0.82 ± 0.21		
	20.8	5	1.08 ± 0.08		
	24.8	10	1.15 ± 0.09		
Br_2	10.5	8	0.97 ± 0.09	$12.3\pm\ 5.6$	$-201\ \pm19$
	15.4	8	1.11 ± 0.03		
	20.2	8	1.24 ± 0.07		
	25.4	9	1.31 ± 0.08		

a) Errors quoted are standard deviations.

mediates, however, **2** is more appealing since it requires a less reorganization of atoms, followed by reductive elimination at the gold(III) center to afford the final product, $[Au(n\text{-}Bu_2dtc)_2][AuX_2]$.

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References

1) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1970), and references cited therein.

2) J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, *Structure and Bonding*, **28**, 83 (1976), and references cited therein.

3) E. A. Pasek and D. K. Straub, *Inorg. Chim. Acta*, **21**, 23 (1977).

4) B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, **16**, 488 (1977).

5) H. Kita, K. Tanaka, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 2816 (1975).

6) H. Kita, K. Tanaka, and T. Tanaka, *Inorg. Chim. Acta*, **21**, 229 (1977).

7) H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organomet. Chem.*, **2**, 236 (1964).

8) P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

9) S. Åkerström, *Arkiv Kemi*, **14**, 387 (1959).

10) J. A. Riddick and E. E. Toops Jr., "Technique of Organic Chemistry," 2nd ed, ed by A. Weissberger, Interscience Publishers, New York (1955), Vol. 7, p. 409.

11) S. Åkerström, *Arkiv Kemi*, **14**, 403 (1959); and T. Vangard and S. Åkerström, *Nature*, **184**, 183 (1959).

12) R. Hesse and P. Jennische, *Acta Chem. Scand.*, **26**, 3855 (1972).

13) A. F. Grand and M. Tamres, *Inorg. Chem.*, **8**, 2459 (1969).

14) R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).

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

16) G. Reichenbach, S. Santini, and U. Mazzucato, *J. Chem. Soc., Faraday Trans. 1*, **69**, 143 (1973).

17) M. Tamres, "Molecular Complexes," ed by R. Foster, Paul Elek Ltd, London (1973), Vol. 1, p. 98.

18) A. L. Balch and D. J. Doonan, *J. Organomet. Chem.*, **131**, 137 (1977).

19) H. Schmidbaur and R. Franke, *Inorg. Chim. Acta*, **13**, 85 (1975); H. Schmidbaur, J. R. Mandl, A. Frank, and G. Huttner, *Chem. Ber.*, **109**, 466 (1976).