1872 © *1991 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 64, 1872—1877 (1991)* [Vol. 64, No. 6

# Kinetics and Mechanisms of Photo-Induced Reduction of Iodine by Diamine-*N*-polycarboxylate Ions in an Aqueous Solution

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(Received February 5, 1991)

Although the reduction of iodine by diamine-*N*-polycarboxylate ions such as ethylenediaminetetraacetic acid, *trans*-1,2-cyclohexanediaminetetraacetic acid, *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid, and ethylenediamine-*N,N'*-diacetic acid was negligible in the dark, it occurred greatly upon irradiation with visible light of an aqueous solution over the pH range 4—8. The rate of the photo-sensitized reaction was of half-order regarding both the light intensity irradiated and the concentrations of iodine, which correspond to those of the triiodide ion in the presence of excess iodide ions, and was proportional to the concentration of the diamine-*N*-polycarboxylate ion. Further, the rate was of half-order for concentrations of $I^-$ below $3\times10^{-4}$ mol dm$^{-3}$ and was of inversely half-order for concentrations of $I^-$ above $6\times10^{-4}$ mol dm$^{-3}$. The reaction was inhibited by radical scavengers of acrylonitrile, acrylamide, and hexaamminecobalt(III) ions. Both hydrogen ion and complex-forming metal ions, such as copper(II) and zinc(II), are also strong inhibitors of the reaction. The reaction mechanism, where initiation reaction is a photo-dissociation of iodine and the reactive species is a $I_2^{\cdot-}$ radical anion, is proposed to account for the obtained results.

Previously, the photo-chemical reaction between ethylenediaminetetraacetic acid ($H_4$edta) and iodine ($I_2$) was used for the analytical chemistry determination of trace amounts of the nitrite ion.[1] The photoreduction mechanism of iodine by amine-*N*-polycarboxylic acid has been proposed based on an initial photodissociation of iodine to iodine atoms followed by chain propagation.[2] In the absence of iodide ions an induction period is present in the photoreduction of iodine by ethylenediaminetetraacetic acid; the reaction occurs with the production of $I^-$ ions.[1,2] When high concentrations of $I^-$ ions were used, the reduction of iodine by oxalate ions was inhibited by $I^-$ ions.[3] Such an effect of the $I^-$ ions on the reduction of iodine cannot be explained by the above proposed mechanism. We have reported that, under the condition that $[I_2]\ll[I^-]$, a full kinetic treatment is possible for a photo-induced reduction of iodine by oxalate ions by monitoring the decay of $I_3^-$.[3] To clarify the mechanisms of the oxidation of amine-*N*-polycarboxylate ions and of the reduction of iodine, we report in this study on the photo-induced reduction of iodine by amine-*N*-polycarboxylate ions in the presence of the $I^-$ ion.

## Experimental

**Chemicals.** Iodine, potassium iodide, $Na_2H_2$edta,[4] $H_4$cdta (=*trans*-1,2-cyclohexanediaminetetraacetic acid),[4] $H_3$hedta (=*N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid),[4] $H_2$edda (=ethylenediamine-*N,N'*-diacetic acid),[4] and the other chemicals used were of guaranteed reagent grade from Wako Pure Chemical Industries, Ltd. All of the solutions were prepared from redistilled water. The pH's of the solutions were adjusted with an acetate buffer (pH 3.5—6.5), a phosphate buffer (pH 6.5—8), and sulfuric acid (below pH 3.5). No effect of anions in the buffers was observed on the kinetic results.

**Procedure.** The kinetic measurements employed were the same as those in the method reported previously.[3] Each sample solution was continuously irradiated with visible light from two 100-W tungsten lamps. Aliquot samples were withdrawn at appropriate time intervals after starting the reaction; the absorbance at 350 nm due to $I_3^-$ ($\varepsilon$ $2.5\times10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)[3] was measured by Shimadzu UV-200S and UV-150-02 spectrophotometers. All of the kinetic runs were followed under the condition that the iodide ions had at least a 50-fold excess over iodine. When solutions prepared from nitrogen-saturated water were used, the kinetic results were the same as those in air-saturated solutions. Thus, all of the kinetic measurements were carried out in air-saturated solutions. The temperature was controlled within 0.1 °C. The light intensity was determined using potassium tris(oxalato)ferrate(III) trihydrate as an actinometer.[5] The iron(II) content was determined spectrophotometrically in the form of tris(1,10-phenanthroline)iron(II) ions at 510 nm with a molar absorption coefficient of $1.1\times10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$.

## Results and Discussion

Although the redox reaction between iodine and diamine-*N*-polycarboxylic acid was practically negligible in the dark, it occurred greatly upon irradiation with visible light of the aqueous solutions over the pH range 4—8. Iodine was rapidly converted to $I_3^-$ in the presence of $I^-$:[6,7]

$$I_2 + I^- \rightleftarrows I_3^-, \qquad (1)$$

where $k_f=5.6\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and $K_1=7.1\times10^2$ dm$^3$ mol$^{-1}$. The absorbance of $I_3^-$ at 350 nm, where the absorbance due to $I_2$ was quite negligible, was used as a monitor for the kinetic measurements in the present study. A half-order plot for the reaction based on Eq. 2 was linear up to almost completion of the reaction (Fig. 1):

$$A_t^{1/2} - A_0^{1/2} = -(1/2)(\varepsilon l)^{1/2}\, k_{\mathrm{obsd}}t, \qquad (2)$$

where $A_0$ and $A_t$ represent the absorbance at zero time and $t$, respectively, $\varepsilon$ is the molar absorption coefficient of $I_3^-$ at 350 nm, and $l$ is the optical path length to be 1

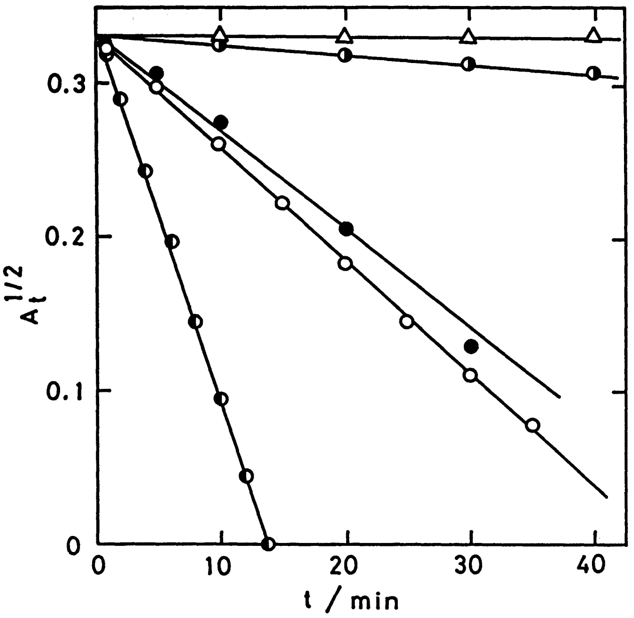


Fig. 1. The half-order plots of $A_t^{1/2}$ vs. $t$ for the photoreaction of iodine with diamine-*N*-polycarboxylate ions and ethylenediamine. $[I_2]=1.0\times10^{-5}$ mol dm$^{-3}$, $[I^-]_0=1.0\times10^{-3}$, mol dm$^{-3}$, [diamine-*N*-polycarboxylate]$_0=1.0\times10^{-4}$ mol dm$^{-3}$, and $I_0=1.41\times10^{-7}$ mol dm$^{-3}$ s$^{-1}$ at 25 °C and pH 4.62 (a 0.1 mol dm$^{-3}$ acetate buffer). ○: EDTA, ●: CDTA, ◐; HEDTA, ◑: EDDA, and △: ethylenediamine.

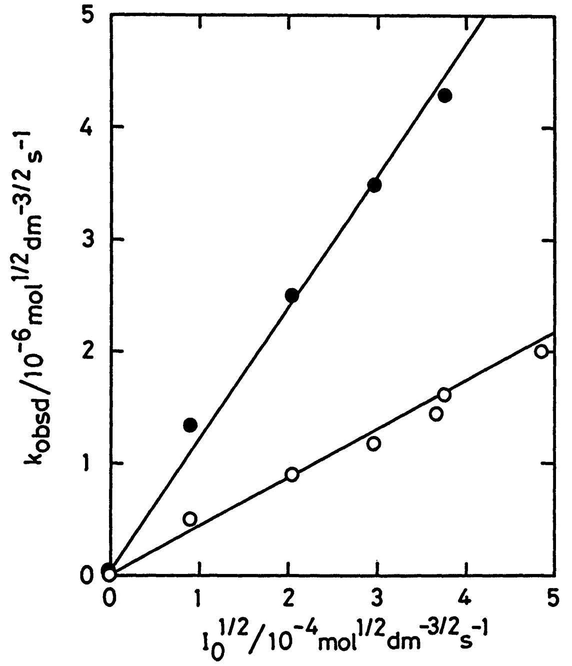


Fig. 2. Plots of $k_{obsd}$ vs. $I_0^{1/2}$ for the photoreaction of iodine with EDTA. ○: $[EDTA]_0=1.0\times10^{-4}$ mol dm$^{-3}$ at pH 4.62 (a 0.1 mol dm$^{-3}$ acetate buffer) and ●: $[EDTA]_0=1.0\times10^{-5}$ mol dm$^{-3}$ at pH 8.6 (a 0.1 mol dm$^{-3}$ phosphate buffer). Other conditions are the same as in Fig. 1.

cm in the present study. Thus, the rate law is described as in Eq. 3:

$$-d[I_3^-]/dt = k_{obsd}[I_3^-]^{1/2}. \tag{3}$$

**Effect of Light Intensity.** The observed rate constant ($k_{obsd}$) increased with an increase in the light intensity irradiated ($I_0$) and plots of $k_{obsd}$ vs. $I_0^{1/2}$ were rectilinear with zero intercept (Fig. 2). These results show that the reacting species is either $I^\bullet$ or/and $I_2^{\bullet-}$ dissociated by light irradiation of the $I_2$ molecule.[3] The latter species is produced successively by a reaction between $I^\bullet$ and $I^-$:

$$I_2 \overset{h\nu}{\rightleftarrows} 2I^\bullet \quad [k_{-4}=8\times10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}],^{8)} \tag{4}$$

$$I^\bullet + I^- \rightleftarrows I_2^{\bullet-} \quad [K_5=1.1\times10^4\ \mathrm{dm^3\,mol^{-1}}].^{9,10)} \tag{5}$$

**Concentration Dependence of Diamine-*N*-polycarboxylate.** The rate of photoreduction of iodine increased proportionally to the concentrations of the diamine-*N*-polycarboxylate ions. Plots of $k_{obsd}$ vs. the initial concentrations of EDTA ($[EDTA]_0$) are shown in Fig. 3. This fact indicates that the reaction of $I^\bullet$ or $I_2^{\bullet-}$ with EDTA is rate determining.

**Effect of the Iodide Ion Concentration.** The rate of the reaction increased with increasing the concentrations of $I^-$ ions up to about $4\times10^{-4}$ mol dm$^{-3}$ and then decreased (Fig. 4). This fact, together with the observation of a half-order dependence of $[I_3^-]$ on the rate, shows that the reaction of $I^\bullet$ is negligible and that the reactive species is $I_2^{\bullet-}$, since the reaction in the absence of $I^-$ is very slow.

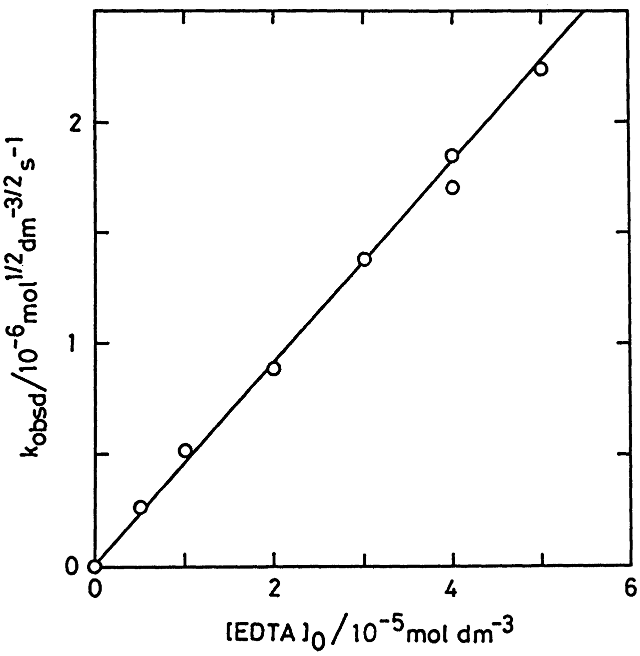


Fig. 3. Plots of $k_{obsd}$ vs. $[EDTA]_0$ for the photoreaction of iodine with EDTA at 35 °C. Other conditions are the same as in Fig. 1.

**pH Dependence.** The photoreduction of iodine by diamine-*N*-polycarboxylate ions was very slow at any pH less than 2. The reaction rate increased markedly

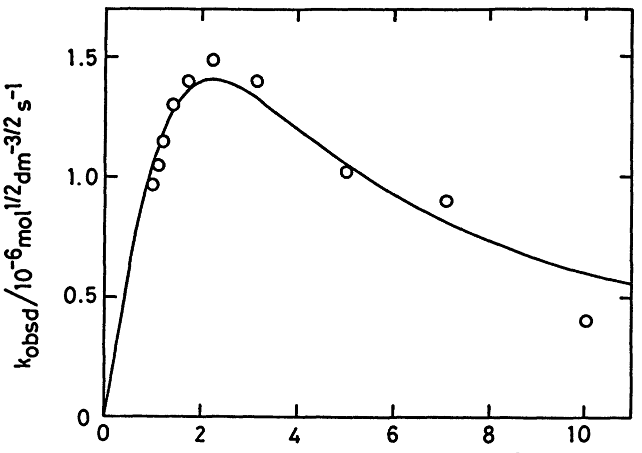


Fig. 4. Plots of $k_{obsd}$ vs. $[I^-]_0^{1/2}$ for the photoreaction of iodine with EDTA. Conditions are the same as in Fig. 1.

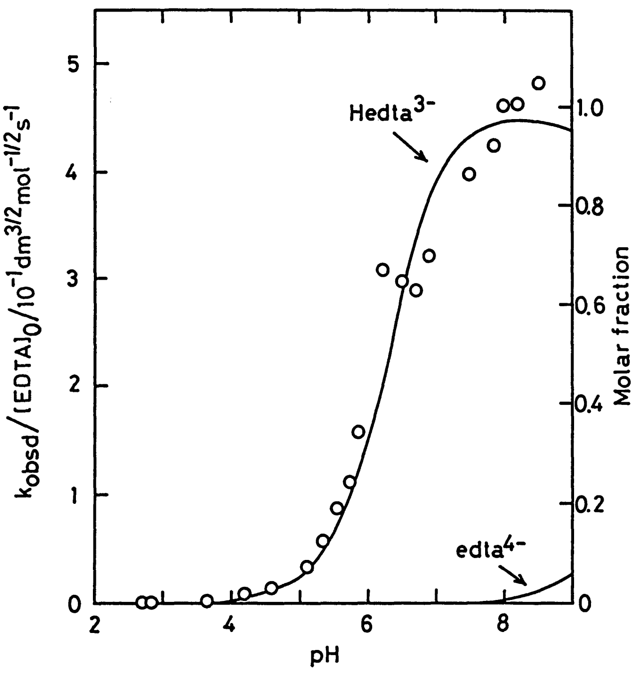


Fig. 5. Plots of $k_{obsd}$ vs. pH for the photoreaction of iodine with EDTA and the molar fraction curve (the solid lines) for $Hedta^{3-}$ and $edta^{4-}$ against pH as indicated. Conditions are the same as in Fig. 1.

with increasing pH at 5—8. Such a pH-dependent curve for the reaction rate superimposes the molar fraction curve for the species $Hedta^{3-}$ (Fig. 5). Thus, the species of $Hedta^{3-}$ could be a main reductant for the radical $I_2^{\cdot -}$ and the other protonated species $H_2edta^{2-}$, $H_3edta^-$, and $H_4edta$ would be quite inactive. The species of $edta^{4-}$ may be more reactive than the $Hedta^{3-}$ ion, but the $edta^{4-}$ ion is negligible below pH 8 (see Fig. 5). Consequently, the following equation can be assumed:

Table 1. Effect of Radical Scavengers for the Photoreaction of Iodine with EDTA at $1.0\times10^{-4}$ mol dm$^{-3}$. Other Conditions are the Same as in Fig. 1

| [Scavenger]/mol dm$^{-3}$ | $k_{obsd}/10^{-6}$ mol$^{1/2}$ dm$^{-3/2}$ s$^{-1}$ |
|---|---|
| 0 | 1.30 |
| Acrylonitrile | |
| 0.090 | 1.09 |
| 0.19 | 0.78 |
| 0.28 | 0.65 |
| Acrylamide | |
| 0.070 | 1.09 |
| 0.14 | 0.82 |
| 0.21 | 0.71 |
| $[Co(NH_3)_6]^{3+}$ | |
| $1.0\times10^{-4}$ | 1.11 |
| $2.0\times10^{-4}$ | 0.89 |
| $5.0\times10^{-4}$ | 0.64 |
| $1.0\times10^{-3}$ | 0.52 |

$$k_{obsd} = k[Hedta^{3-}] = k[EDTA]_0/\alpha_{HY}, \quad (6)$$

where $\alpha_{HY}$ is a side reaction coefficient $(1+K_{a4}/[H^+]+[H^+]/K_{a3}+[H^+]^2/K_{a2}K_{a3}+[H^+]^3/K_{a1}K_{a2}K_{a3})$ and $K_{a1}$, $K_{a2}$, $K_{a3}$, and $K_{a4}$ are stepwise acid-dissociation constants of $H_4edta$ ($pK_{a1}=2.07$, $pK_{a2}=2.75$, $pK_{a3}=6.24$, and $pK_{a4}=10.34$ at 25 °C and $I=0.1$ mol dm$^{-3}$).[11]

For the EDDA system the values of $k_{obsd}/[EDDA]_0$ at pH 4.62, 5.60, 6.49, and 7.20 were $1.35\times10^{-3}$, $6.11\times10^{-3}$, $2.13\times10^{-2}$, and $1.00\times10^{-1}$ dm$^{3/2}$ mol$^{-1/2}$ s$^{-1}$, respectively. These data did not fit to the molar fraction curve for the only $Hedda^-$ species at higher pH, being different from the EDTA system. The reason is discussed later.

**Effect of Radical Scavenger.** The addition of a radical scavenger, acrylonitrile or acrylamide, into the reaction solution decreased the photoreduction rate of iodine. The value of $k_{obsd}$ in the presence of 1.0—1.5% of the radical scavenger reached about half value in the absence of a radical scavenger (Table 1). In the presence of a radical scavenger and in the absence of EDTA, the absorbance of $I_3^-$ did not decrease appreciably. Thus, it is assumed that the acrylonitrile or acrylamide monomer does not react with $I_3^-$, $I_2$, $I^\cdot$, and $I_2^{\cdot -}$, but reacts with the photo-oxidizing products of EDTA. Considering that the decrease in $k_{obsd}$ is dependent on the amounts of the radical scavenger, it is also likely that the photo-oxidizing products of EDTA are able to reduce $I_2$ and/or $I_3^-$, competing with the radical scavenger.

It is found that a hexaamminecobalt(III) ion ($[Co(NH_3)_6]^{3+}$) also decreases the rate of the reaction, and that the value of $k_{obsd}$ reaches about half in the absence of $[Co(NH_3)_6]^{3+}$ ions (Table 1). Without amine-*N*-polycarboxylate ions the photoreaction did not occur at pH 4—8, suggesting that the $[Co(NH_3)_6]^{3+}$ ions are quite inactive to the reducing radical anion $I_2^{\cdot -}$. This is reasonable on the basis of the redox potentials for these species:[12,13] $E^0([Co(NH_3)_6]^{3+/2+})=0.06$ V and $E^0(I_2/I_2^{\cdot -})=0.21$ V.

**Temperature Dependence.** The temperature dependence on the rate was examined under the same condi-

Table 2. Temperature Dependence on the Observed Rate Constant ($k_{\mathrm{obsd}}$) for the Photoreaction of Iodine with EDTA at $4.0\times10^{-5}$ mol dm$^{-3}$. Other Conditions are the Same as in Fig. 1

| Temp/°C | $k_{\mathrm{obsd}}/10^{-6}$ mol$^{1/2}$ dm$^{-3/2}$ s$^{-1}$ |
|---|---|
| 10.0 | 0.14 |
| 15.0 | 0.25 |
| 25.0 | 0.72 |
| 30.0 | 1.10 |
| 35.0 | 1.77 |

tions as are shown in Fig. 1, except for $[\mathrm{EDTA}]_0=4.0\times10^{-5}$ mol dm$^{-3}$ with various temperatures over 10—35 °C. The results are given in Table 2. The enthalpy and entropy changes of activation were determined from the plots of $\log(k_{\mathrm{obsd}}/T)$ vs. $T^{-1}$ ($\Delta H^{\ddagger}=72.1\pm3.6$ kJ mol$^{-1}$ and $\Delta S^{\ddagger}=-121\pm10$ J K$^{-1}$ mol$^{-1}$).

**Mechanism of Reaction.** The obtained results are well accounted for by the following mechanism after Reactions 1, 4, and 5 occurred:

$$\mathrm{I_2^{\overline{\cdot}}} + \mathrm{Y} \xrightarrow{k_7} 2\mathrm{I^-} + \mathrm{Y^{\dot{+}}} \tag{7}$$

and

$$\mathrm{I_2\ (or\ I_3^-)} + \mathrm{Y^{\dot{+}}} \xrightarrow{\text{fast}} \text{products}, \tag{8}$$

where Y represents the amine-*N*-polycarboxylate ions. Assuming a steady-state concentration for I•,

$$I_a\phi + k_{-5}[\mathrm{I_2^{\overline{\cdot}}}] - k_{-4}[\mathrm{I^{\bullet}}]^2 - k_5[\mathrm{I^{\bullet}}][\mathrm{I^-}] = 0, \tag{9}$$

where $I_a$ and $\phi$ are the light intensity absorbed and quantum yield, respectively. Under equilibrium conditions of $k_{-5}[\mathrm{I_2^{\overline{\cdot}}}]=k_5[\mathrm{I^-}][\mathrm{I^{\bullet}}]$,

$$[\mathrm{I^{\bullet}}] = (I_a\phi/k_{-4})^{1/2}. \tag{10}$$

Under an excess concentration of I$^-$, $[\mathrm{I^{\bullet}}]=[\mathrm{I_2^{\overline{\cdot}}}]$, where

$$[\mathrm{I_2^{\overline{\cdot}}}] = (I_a\phi/k_{-4})^{1/2}. \tag{11}$$

Under the condition $[\mathrm{I^{\bullet}}]_{\mathrm{total}}=[\mathrm{I^{\bullet}}]+[\mathrm{I_2^{\overline{\cdot}}}]$,

$$[\mathrm{I_2^{\overline{\cdot}}}] = \frac{[\mathrm{I^{\bullet}}]_{\mathrm{total}}K_5[\mathrm{I^-}]}{1+K_5[\mathrm{I^-}]} \tag{12}$$

and

$$[\mathrm{I_2^{\overline{\cdot}}}] = \left(\frac{I_a\phi}{k_{-4}}\right)^{1/2}\left(\frac{K_5[\mathrm{I^-}]}{1+K_5[\mathrm{I^-}]}\right). \tag{13}$$

Therefore, the following rate law can be derived:

$$-\frac{\mathrm{d}[\mathrm{I_3^-}]}{\mathrm{d}t} = \frac{k_7}{2}\left(\frac{I_a\phi}{k_{-4}}\right)^{1/2}\left(\frac{K_5[\mathrm{I^-}]}{1+K_5[\mathrm{I^-}]}\right)[\mathrm{Y}]. \tag{14}$$

From Lambert-Beer's law $I_a$ correlates to an incident light intensity ($I_0$) with iodine concentrations of

$$I_a = I_0[1-\exp(-\alpha[\mathrm{I_2}])], \tag{15}$$

where $\alpha$ is a constant containing an absorption coefficient and an optical path length. Under the condition $\alpha[\mathrm{I_2}]<0.1$ employed in this study, Eq. 15 can be simplified to

$$I_a = I_0\alpha[\mathrm{I_2}]. \tag{16}$$

Therefore, Eq. 14 can be represented as

$$-\frac{\mathrm{d}[\mathrm{I_3^-}]}{\mathrm{d}t} = \frac{k_7}{2}\left(\frac{I_0\alpha\phi}{k_{-4}K_1}\right)^{1/2}\left(\frac{[\mathrm{I_3^-}]}{[\mathrm{I^-}]}\right)^{1/2}\left(\frac{K_5[\mathrm{I^-}]}{1+K_5[\mathrm{I^-}]}\right)[\mathrm{Y}], \tag{17}$$

$$k_{\mathrm{obsd}} = \frac{k_7}{2}\left(\frac{I_0\alpha\phi}{k_{-4}K_1}\right)^{1/2}\left(\frac{K_5[\mathrm{I^-}]^{1/2}}{1+K_5[\mathrm{I^-}]}\right)[\mathrm{Y}], \tag{18}$$

The values of $\alpha$ and $k_7$ could not be obtained in this work, although the values of $\phi$ and $k_{-4}$ are known ($\phi=0.11$—$0.83$ and $k_{-4}=8\times10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$).

The following reaction for the initial photoreaction is also possible:[9]

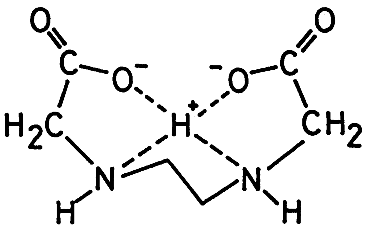
$$\mathrm{I_3^-} \xrightleftharpoons{h\nu} \mathrm{I_2^{\overline{\cdot}}} + \mathrm{I^{\bullet}}. \tag{19}$$

The results at low concentrations of I$^-$, where the rate is dependent on $[\mathrm{I^-}]^{1/2}$, could be well accounted for by Reaction 19. The solid curve in Fig. 4 was calculated by using $K_5=2\times10^3$ dm$^3$ mol$^{-1}$ and $k_7(\alpha\phi)^{1/2}=8.0\times10^6$ dm$^{9/2}$ mol$^{-3/2}$ s$^{-1}$. The estimated value for $K_5$ is smaller than that reported previously.[9,10] This may be attributable to the different experimental conditions or to the contribution of the bimolecular decay of the $\mathrm{I_2^{\overline{\cdot}}}$ ions:

$$2\mathrm{I_2^{\overline{\cdot}}} \longrightarrow \mathrm{I_3^-} + \mathrm{I^-} \quad [k_{20}=4.5\times10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}].^{15)} \tag{20}$$

The reaction of I• with EDTA and other diamine-*N*-polycarboxylate ions must be neglected on the basis of the [I$^-$] dependence.

**Effect of Diamine-*N*-polycarboxylate.** The pH dependence on the reaction rate of EDTA indicates that at least one proton-free nitrogen in the molecule is required for the reduction of the radical species, $\mathrm{I_2^{\overline{\cdot}}}$, and that the lone electron-pair on the nitrogen atom is available for electron transfer to the $\mathrm{I_2^{\overline{\cdot}}}$ radical anion. The rate constants ($k_{\mathrm{obsd}}/[\text{amine-}N\text{-polycarboxylate}]_0$) under completely same conditions were $1.35\times10^{-3}$, $1.30\times10^{-2}$, $1.45\times10^{-2}$, and $4.90\times10^{-2}$ dm$^{3/2}$ mol$^{-1/2}$ s$^{-1}$ at pH 4.62 for EDDA, CDTA, EDTA, and HEDTA, respectively. The trend in reactivity, EDDA$\ll$CDTA$\approx$EDTA$<$HEDTA, is the same as that for the acid-dissociation constants of these amine-*N*-polycarboxylate ions,[11] H$_2$edda (p$K_{\mathrm{a1}}$=6.48)<H$_4$cdta (p$K_{\mathrm{a3}}$=6.20)≈H$_4$edta (p$K_{\mathrm{a3}}$=6.24)<H$_3$hedta (p$K_{\mathrm{a2}}$=5.41), respectively; it is noted that the EDDA system is exceptionally slow. Under the same conditions as in Fig. 1 (but at pH 7.2), the rate for EDDA increased to 70-fold in $k_{\mathrm{obsd}}/[\mathrm{EDDA}]_0$ ($1.00\times10^{-1}$ dm$^{3/2}$ mol$^{-1/2}$ s$^{-1}$). This suggests that edda$^{2-}$ is more reactive than Hedda$^-$, the latter being less reactive than Hedta$^{3-}$. Chapman et al.[16] demonstrated from IR and NMR studies of Hedta$^{3-}$ in an aqueous solution that two of the carboxylate groups of Hedta$^{3-}$ are hydrogen-bonded to one N$^+$H and that the other two are free. Therefore, the free nitrogen may be reactive with $\mathrm{I_2^{\overline{\cdot}}}$ in the Hedta$^{3-}$ ion. The inactivity of the species, Hedda$^-$, may arise from the fact that both carboxylate groups of Hedda$^-$ are possible to be hydrogen-bonded to N$^+$H in solutions.



Hedda$^-$

**Effect of Metal Ion.** In order to confirm the importance of the lone electron-pair on the amino groups in amine-*N*-polycarboxylate ions mentioned above, we examined the effect of metal ions and found that those which were able to form chelate compounds with the diamine-*N*-polycarboxylate ions, greatly inhibited the photoreduction of iodine. The rate law of Eq. 3 was always satisfied for the coexistence of any metal ions employed. Plots of $k_{obsd}$ vs. $[M^{2+}]_0/[EDTA]_0$ are given in Fig. 6. Strong complex-forming ions, such as copper(II) and zinc(II), inhibit quantitatively, while relatively weak complex-forming ions, such as magnesium(II) and calcium(II), can not greatly inhibit the photoreduction of iodine at pH 4.62. For example, even in a $10^3$-fold excess of magnesium over EDTA, the decrease in $k_{obsd}$ was only 20% of that in the absence of the metal ion. The trend regarding the inhibitory effect on the rate at pH 4.62 is $Mg^{2+} < Ca^{2+} \ll Zn^{2+} \approx Cu^{2+}$, the order of which is the same as that of the stability constants of the chelate complex $[M(edta)]^{2-}$; the values of $\log K_{M(edta)}$ at 25 °C and $I$=0.1 mol dm$^{-3}$ are 8.7, 10.6, 16.4, and 18.7 for $Mg^{2+}$, $Ca^{2+}$, $Zn^{2+}$, and $Cu^{2+}$, respectively.[10] The results in Fig. 6 indicate that the chelated metal(II) ions cannot reduce any radicals of $I_2^{\cdot -}$ and $I^{\cdot}$ in the case of Cu(II) and Zn(II) ions. Lati and Meyerstein[17] have reported that $[Cu(edta)]^{2-}$ did not react with the $I_2^{\cdot -}$ produced by electron pulse radiolysis. Therefore, the lone electron pair on the nitrogen atom must play an important role in the oxidation and fragmentation of any amine-*N*-polycarboxylate ions.

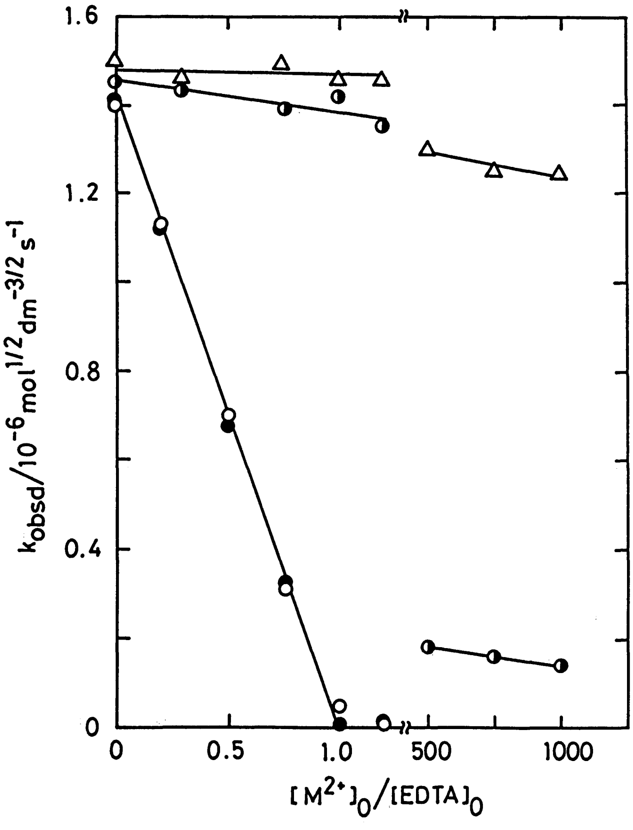


Fig. 6. Plots of $k_{obsd}$ vs. $[M^{2+}]_0/[EDTA]_0$ for the photoreaction of iodine with EDTA. Conditions are the same as in Fig. 1. ○: $Cu^{2+}$, ●: $Zn^{2+}$, ◑; $Ca^{2+}$, and △: $Mg^{2+}$ for $M^{2+}$ ions.

The fragmentation of EDTA in thermal reactions is complicated and the reaction mechanism is still unclear. It has been reported that $CO_2$ and HCHO are detected as products.[18] We found $CO_2$ as one of the products in the photoreduction of iodine by EDTA, and also examined the stoichiometry of the reaction. Under the condition $[I_2] \gg [EDTA]_0$, the stoichiometry was not 1 : 1; more than one mole of $I_2$ was consumed against EDTA. An accurate stoichiometric number could not be determined, but seemed to certainly be dependent on the pH of the reacting solution. Since ethylenediamine was completely inactive under the present experimental conditions (see Fig. 1), fragmentation must occur at acetate arms of EDTA. An ESR study by Poupko et al.[19] has shown that the hydrogen abstraction from EDTA occurs at the acetate carbon atom adjacent to nitrogen atom. Under the condition $[EDTA]_0 \gg [I_2]$, which was employed in the present study, fragmentation might have occurred at one acetate group. The effect of radical scavengers of acrylonitrile or $[Co(NH_3)_6]^{3+}$ for the photooxidation of EDTA is completely different from that for the oxalate system studied previously,[3] the latter having a $CO_2^{\cdot -}$ radical anion as an intermediate. This fact suggests that the intermediate radical species is not a free $CO_2^{\cdot -}$ in Reaction 7, but that the radical ion $Y^{\cdot +}$ still holds the $-CO_2$ fragment.

In conclusion, we demonstrated that the photoreduction of iodine with diamine-*N*-polycarboxylate ions in an aqueous solution occurs in the order of the reaction rate, HEDTA>EDTA≈CDTA≫EDDA, and that the lone electron-pair of the nitrogen atom plays an important role in the oxidation and fragmentation of amine-*N*-polycarboxylate ions.

This research was supported by a Grant-in-Aid for Scientific Research No. 01470051 from the Ministry of Education, Science and Culture.

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4) The symbols, EDTA, CDTA, HEDTA, and EDDA are abbreviated for all the forms of $H_n$edta$^{(4-n)-}$ ($n$=0—4), $H_n$cdta$^{(4-n)-}$ ($n$=0—4), $H_n$hedta$^{(3-n)-}$ ($n$=0—3), and $H_n$edda$^{(2-n)-}$ ($n$=0—2), respectively.

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