Bull. Chem. Soc. Jpn., 65, 1812—1816 (1992) [Vol. 65, No. 7

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

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(Received January 27, 1992)

The photo-induced reduction kinetics of iodine by monoamine-*N*-polycarboxylate ions, such as nitrilotriacetic acid (H_3nta), iminodiacetic acid (H_2ida), 2-hydroxyethyliminodiacetic acid (H_2hida), as well as *o*-, *m*-, and *p*-isomers of *N*-(carboxyphenyl)iminodiacetic acid (H_3cpida), were made in an aqueous solution containing iodide ions in excess over the pH range 1.6—7.6; the photo-induced reductions of iodine by triethylamine (TEA) and tris(2-hydroxyethyl)amine (TEOA) were also studied. The reactive species are a $I_2^{\bar{\cdot}}$ radical anion, produced in the primary photoreaction, and a fully deprotonated species of monoamine-*N*-polycarboxylate, TEOA, or TEA. Both hydrogen ion and complex-forming metal ions, such as copper(II) and zinc(II), were strong inhibitors for all of the reactions investigated. The role of the lone electron pair on the amine nitrogen is discussed.

The photo-chemical reaction of polyamine-*N*-polycarboxylate ions with iodine has been studied in an aqueous solution.[1-3] We demonstrated that the reactive species are a $I_2^{\bar{\cdot}}$ radical anion, formed in the primary photo-dissociation process of iodine in the presence of iodide ions, and a monoprotonated form of ethylenediaminetetraacetic acid (Hedta^{3-}).[3] It is suggested that the fully deprotonated species, edta^{4-}, is more reactive than the Hedta^{3-} ion, and that the lone electron-pair on the amine nitrogen plays an important role in the oxidation and fragmentation of amine-*N*-polycarboxylate ions.[3] We thus intended to make a comparison between the diamine-*N*-polycarboxylic acids, such as ethylenediaminetetraacetic acid (H_4edta) and the monoamine-*N*-polycarboxylic acid (such as nitrilotriacetic acid (H_3nta), iminodiacetic acid (H_2ida), 2-hydroxyethyliminodiacetic acid (H_2hida), as well as *o*-, *m*-, and *p*-isomers of *N*-(carboxyphenyl)iminodiacetic acid (H_3cpida)). Further, in order to clarify the role of the carboxylate function in the amine molecule, we also examined the photo-induced reduction of iodine using amines without involving carboxylic acid, such as tris(2-hydroxyethyl)amine (TEOA) and triethylamine (TEA).

Experimental

Chemicals. Iodine, potassium iodide, monoamine-*N*-polycarboxylic acid (H_3nta, H_2hida, and H_2ida), tris(2-hydroxyethyl)ammonium dihydrogenphosphate ([Hteoa]H_2PO_4), and triethylammonium chloride ([Htea]Cl) were purchased from Wako Pure Chemical Industries, Ltd. The *o*-, *m*-, and *p*-isomers of *N*-(carboxyphenyl)iminodiacetic acid were prepared from aminobenzoic acid with bromoacetic acid by a previously reported method.[4] The purity was checked by the 270 MHz ^{1}H NMR spectra. The other chemicals used were of guaranteed reagent grade. All of the solutions were prepared by using 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—7.6), and sulfuric acid (below pH 3.5).

Procedure. The kinetic measurements employed were the same as those used in a previously reported method.[3] The solution was continuously irradiated with visible light by means of two 100-W tungsten lamps. Aliquot solutions were withdrawn at appropriate time intervals after starting the reaction; the absorbance at 350 nm, due to I_3^- ($\varepsilon = 2.5\times10^4$ M^{-1} cm^{-1}; 1 M=1 mol dm^{-3}),[5] was measured by a Shimadzu UV-150-02 spectrophotometer. Iodine (I_2) was rapidly converted to a triiodide ion (I_3^-) in the presence of an iodine ion (I^-):[6,7]

$$I_2 + I^- \rightleftharpoons I_3^-. \tag{1}$$

Here, $k_f = 5.6\times10^9$ M^{-1} s^{-1} and $K_1 = 7.1\times10^2$ M^{-1}. All of the kinetic measurements were carried out in air-saturated solutions under the condition that the iodide ions had at least a 100-fold excess over iodine. The temperature was controlled at 25.0±0.1 °C. The light intensity was determined by using potassium tris(oxalato)ferrate(III) trihydrate as an actinometer in the previously reported method.[3]

Results and Discussion

Since the fragmentation of amine-*N*-polycarboxylate ions is rather complicated,[3] we therefore employed the condition that [amine-*N*-polycarboxylate]$\gg$[I_2] in order to simplify the oxidation of amine-*N*-polycarboxylate ions in this study. A half-order plot for the photo-induced reduction of iodine by monoamine-*N*-polycarboxylate ions, TEOA, or TEA was linear for at least 90% completion of the reaction. Thus, the rate law is described as in Eq. 2, which is the same as that for the diamine-*N*-polycarboxylate systems reported previously:[3]

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

In the case of H_3cpida systems, the linearity of the half-order plot was not good and the rate constant was, therefore, obtained from the initial part (ca. 50%) of the slope.

Effect of Light Intensity. The linear dependence of the observed rate constant (k_{obsd}) on the square root of the light intensity irradiated ($I_0^{1/2}$), as is shown in Fig. 1, confirmed the previous result that the reacting species is $I_2^{\bar{\cdot}}$:[3]

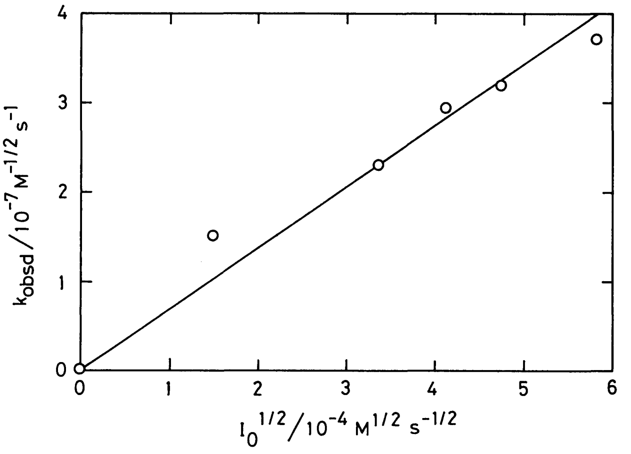


Fig. 1. Plots of k_{obsd} vs. $I_0^{1/2}$ for the photoreduction of iodine by H_3nta. $[I_2]_0=1.00\times10^{-5}$ M, $[I^-]_0=1.00\times10^{-3}$ M, and $[H_3nta]_0=1.00\times10^{-3}$ M at pH 6.00 (a 0.1 M acetate buffer) and 25 °C.

$$I_2 \overset{h\nu}{\rightleftharpoons} 2I\cdot \qquad [k_{-3} = 8\times10^9 \text{ M}^{-1} \text{ s}^{-1}],^{8)} \qquad (3)$$

and

$$I\cdot + I^- \rightleftharpoons I_2^{\cdot-} \qquad [K_4 = 1.1\times10^4 \text{ M}^{-1}].^{9,10)} \qquad (4)$$

Concentration Dependence of Monoamine-*N*-polycarboxylates, TEOA, and TEA. Plots of k_{obsd} vs. the initial concentrations of monoamine-*N*-polycarboxylates, TEOA, and TEA ($[Y]_0$) are rectilinear, as shown in Fig. 2, indicating that the reaction of $I_2^{\cdot-}$ with these substrates (Y) is rate-determining (refer to Eq. 5).

pH Dependence. The reaction rate increased with increasing pH over the range 4—8 for the H_3nta, H_2hida, TEOA, and TEA systems (Fig. 3). The pH dependence of the reaction rate for the H_2ida system was similar to that for the H_3nta system. The solid curves in Fig. 3 were calculated assuming that the reacting species are all fully deprotonated (nta^{3-}, $hida^{2-}$, teoa, and tea). The acid dissociation constants for these compounds were taken from the literature:11) $pK_1=1.89$, $pK_2=2.49$, and $pK_3=9.73$ for H_3nta, $pK_1=1.91$ and $pK_2=8.72$ for H_2hida, $pK_1=8.08$ for $Hteoa^+$, and $pK_1=9.73$ for $Htea^+$.

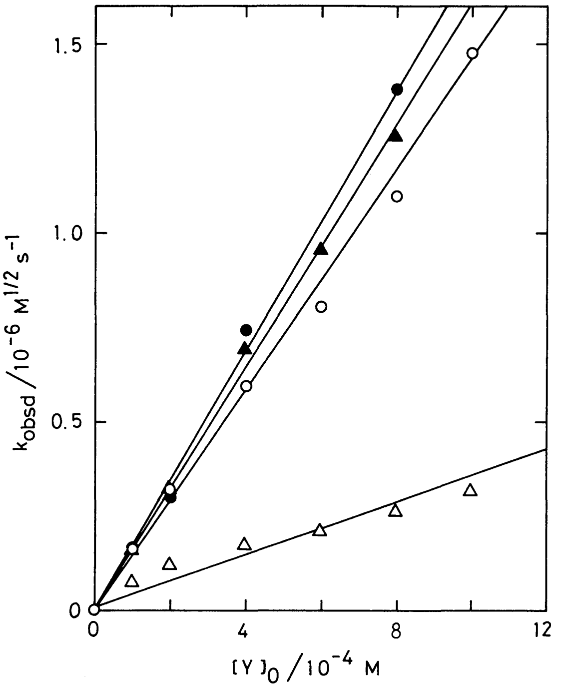


Fig. 2. Plots of k_{obsd} vs. $[Y]_0$ for the photoreduction of iodine by monoamine-*N*-polycarboxylate, TEOA, and TEA at $I_0=1.41\times10^{-7}$ M s^{-1}. ○: H_3nta (pH 4.62), ●: H_2hida (pH 5.60), △: TEOA (pH 4.62), and ▲: TEA (pH 7.90). Other conditions are the same as in Fig. 1.

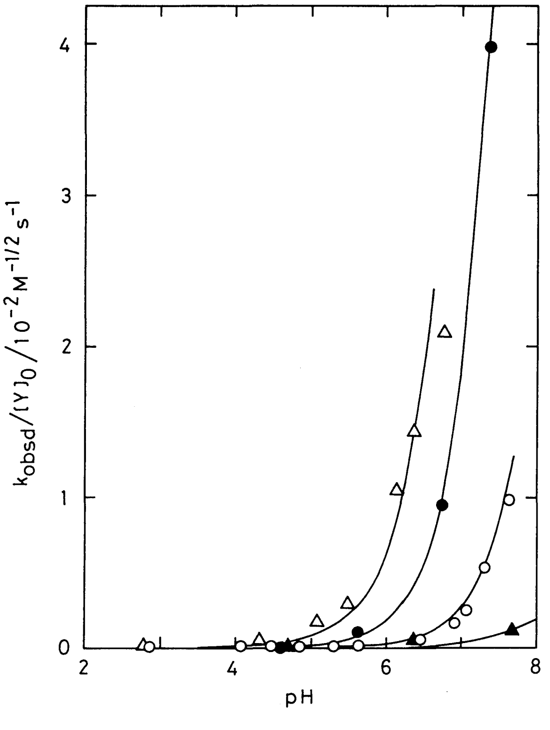


Fig. 3. Plots of $k_{obsd}/[Y]_0$ vs. pH for the photoreduction of iodine by monoamine-*N*-polycarboxylate, TEOA, and TEA. Conditions are the same as in Fig. 2. The solid curves are those calculated (see text). ○: H_3nta, ●: H_2hida, △: TEOA, and ▲: TEA.

In H_3cpida systems the pH dependence of the reaction rate was quite different from that for the H_3nta, H_2hida, TEOA, and TEA systems (Fig. 4). The solid curves fitted to the observed values are calculated based on the assumption that the reacting species are H_2cpida^- ($k_{obsd}/[Y]=0.045$ M$^{-1/2}$ s^{-1}) and $Hcpida^{2-}$ (0.024 M$^{-1/2}$ s^{-1}) for the *o*-isomer, H_3cpida (0.103 M$^{-1/2}$ s^{-1}), H_2cpida^- (0.105 M$^{-1/2}$ s^{-1}), $Hcpida^{2-}$ (0.020 M$^{-1/2}$ s^{-1}), and $cpida^{3-}$ (0.14 M$^{-1/2}$ s^{-1}) for the *m*-isomer, and H_3cpida (0.010 M$^{-1/2}$ s^{-1}), H_2cpida^- (0.035 M$^{-1/2}$ s^{-1}), $Hcpida^{2-}$ (0.035 M$^{-1/2}$ s^{-1}), and $cpida^{3-}$ (0.080 M$^{-1/2}$ s^{-1}) for the *p*-isomer, respectively ($pK_1=2.20$, $pK_2=3.01$, and $pK_3=7.75$ for *o*-H_3cpida; $pK_1=2.40$, $pK_2=4.06$, and $pK_3=5.10$ for *m*-cpida;

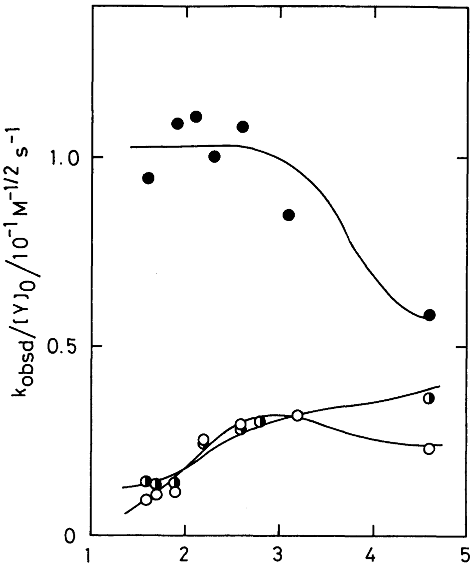


Fig. 4. Plots of $k_{obsd}/[Y]_0$ vs. pH for the photoreduction of iodine by H_3cpida. Conditions are the same as in Fig. 3. The solid curves are those calculated (see text). ○: *o*-H_3cpida, ●: *m*-H_3cpida, and ◐: *p*-H_3cpida.

pK_1=2.31, pK_2=4.28, and pK_3=5.20 for *p*-cpida[11]). The rate constant for *o*-cpida^{3-} could not be determined because of the high pK_3 (7.75) for the *o*-isomer.

Mechanism of Reaction. The observed results are well accounted for by the following mechanism, after Reactions 1, 3, and 4 occurred rapidly:

$$I_2^{-\cdot} + Y \xrightarrow{k_5} 2I^- + Y^{+\cdot} \qquad (5)$$

and

$$I_2(\text{or } I_3^-) + Y^{+\cdot} \xrightarrow{\text{fast}} \text{products.} \qquad (6)$$

Assuming steady-state concentrations of I·, which is thus $I_2^{-\cdot}$ in the presence of iodide ions in large excess and $Y^{+\cdot}$, the following rate law can be derived:[3)]

$$-\frac{d[I_3^-]}{dt} = \frac{k_5}{2}\left(\frac{I_0\alpha\phi}{k_{-3}K_1}\right)^{1/2}\left(\frac{K_4[I^-]^{1/2}}{1+K_4[I^-]}\right)[I_3^-]^{1/2}[Y]. \qquad (7)$$

Here, ϕ and α are the quantum yield and a constant containing the absorption coefficient and the optical path length, respectively. Therefore, the observed rate constant in Eq. 2 can be written as

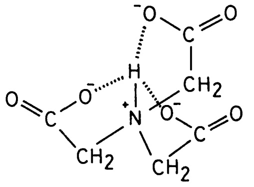
$$k_{obsd} = \frac{k_5}{2}\left(\frac{I_0\alpha\phi}{k_{-3}K_1}\right)^{1/2}\left(\frac{K_4[I^-]^{1/2}}{1+K_4[I^-]}\right)[Y]. \qquad (8)$$

Under the condition that $K_4[I^-] \gg 1$,

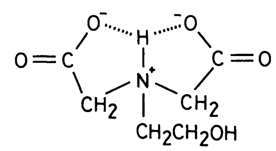
$$k_{obsd} = \frac{k_5}{2}\left(\frac{I_0\alpha\phi}{k_{-3}K_1}\right)^{1/2}[I^-]^{-1/2}[Y]. \qquad (9)$$

Although the dependence of $[I^-]$ on the rate was not examined in the present systems, the results of the diamine-*N*-polycarboxylate system confirmed the above rate law of Eqs. 8 and 9.[3)]

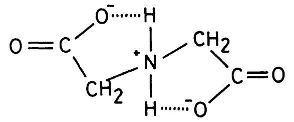
Effect of Monoamine-*N*-polycarboxylates and Amines. The pH dependence on the reaction rate of monoamine-*N*-polycarboxylates indicates that only fully deprotonated species, such as nta^{3-}, hida^{2-}, and ida^{2-}, are active for the oxidation reaction by the radical anion $I_2^{-\cdot}$ (see Eq. 5) and that the monoprotonated species such as Hnta^{2-}, Hhida$^-$, and Hida$^-$ are not active for the oxidation reaction. Consequently, only the free nitrogen atom accompanied by a lone electron-pair in the amine-*N*-polycarboxylate is active for oxidation by the $I_2^{-\cdot}$ ion. This behavior is also consistent with the previous results concerning the diamine-*N*-polycarboxylates.[3)] The inactivity of the Hnta^{2-}, Hhida$^-$, and Hida$^-$ species could result from the following hydrogen-bonding structures of these ions, as has been suggested by an NMR study.[12)] From the data given in Figs. 3 and 4, the rate constants for the deprotonated species, $k_{obsd}/[Y]$ (Y=nta^{3-}, hida^{2-}, ida^{2-}, teoa, cpida^{3-}, and tea), were estimated, and are listed in Table 1. The order of the rate constants, nta^{3-}>ida^{2-}>hida^{2-}>teoa>Hedta^{3-}>*m*-



Hnta^{2-}



Hhida$^-$



Hida$^-$

Table 1. Rate Constants of the Photoreaction of Iodine with Amine-*N*-polycarboxylate, TEOA, and TEA at 25 °C. Conditions are the Same as in Fig. 1

Y	$k_{obsd}/[Y]/M^{-1/2}$ s^{-1}	pK_n
nta^{3-}	1.5	9.73 (*n*=3)
ida^{2-}	1.1	9.13 (*n*=2)
hida^{2-}	0.97	8.72 (*n*=2)
teoa	0.73	8.08 (*n*=1)
Hedta^{3-} a)	0.45	6.24 (*n*=2)
m-cpida^{3-}	0.14	5.10 (*n*=3)
p-cpida^{3-}	0.08	5.20 (*n*=3)
tea	0.11	9.73 (*n*=1)

a) Calculated from the data in Ref. 3.

or *p*-cpida^{3-}>tea, is the same as that of the basicity of the amine nitrogen, except for tea. This strongly suggests the lone electron-pair on the amine nitrogen plays an important role in an electron transfer from the amine nitrogen to $I_2^{\cdot-}$. The exception regarding tea may be ascribable to the absence of acetate and hydroxyethyl groups.

In the case of cpida^{3-}, the oxidation mechanism must be similar to that of the above-mentioned systems. However, the main reacting species are H_2cpida^- and/or $Hcpida^{2-}$ at pH 1.6—4, where the nitrogen atom holds H^+ ions. Therefore, oxidation in these protonated species may not occur at the nitrogen atom, but occurs at the carboxyphenyl group.

Effect of Metal Ion. Plots of $k_{obsd}/[H_3nta]_0$ vs. $[M^{2+}]_0/[H_3nta]_0$ are given in Fig. 5. The trend regarding the inhibitory effect on the rate is $Mg^{2+}<Ca^{2+}\ll Zn^{2+}\approx Cu^{2+}$; this order is the same as that for the stability constants of the chelate complex $[M(nta)]^-$; the values of log $K_{M(nta)}$ at 25 °C and I=0.1 M are 5.46, 6.46, 10.44, and 13.05 for Mg^{2+}, Ca^{2+}, Zn^{2+}, and Cu^{2+}, respectively.[11] Since the formation of $[Cu(nta)]^-$ and $[Zn(nta)]^-$ is quantitative at pH 7.5, inhibition of the reaction by these ions is complete at $[M^{2+}]_0/[Y]_0\geqq 1$. On the other hand, Co^{2+} and Mn^{2+} strongly inhibit the reaction, even at $[M^{2+}]_0/[Y]_0=0.2$. This strongly shows that both the $[Co(nta)]^-$ and $[Mn(nta)]^-$ ions are also oxidized by $I_2^{\cdot-}$. However, when the values of the $[M^{2+}]_0/[H_3nta]_0$ ratio exceeded 0.2, no further inhibition occurred, and the observed rate remained constant. Thus, the $[M^{III}(nta)]$ ions once formed react further with $I_2^{\cdot-}$ to regenerate I_2, constituting the following chain reaction:

$$[M^{II}(nta)]^- + I_2^{\cdot-} \longrightarrow [M^{III}(nta)] + 2I^- \tag{10}$$

$$[M^{III}(nta)] + I_2^{\cdot-} \longrightarrow [M^{II}(nta)]^- + I_2. \tag{11}$$

The rate constants for the photo-reduction of iodine by H_2hida and TEOA in the presence of Cu^{2+}, Zn^{2+}, Mn^{2+}, and Co^{2+} ions are given in Table 2. The trend regarding the inhibitory effect on the rate is $Mn^{2+}<Co^{2+}<Zn^{2+}<Cu^{2+}$, the order of which is the same as that of the stability constants of [M(hida)] or $[M(teoa)]^{2+}$; log $K_{M(hida)}$=6.4 (Mn^{2+}), 9.0 (Co^{2+}), 9.4 (Zn^{2+}), and 11.2 (Cu^{2+}), and log $K_{M(teoa)}$=2.14 (Mn^{2+}), 4.35 (Co^{2+}), and 6.0 (Cu^{2+}), respectively.[11] The Co^{2+} and Mn^{2+} ions did not show a strong inhibitory effect in these systems, contrary to the nta^{3-} system. This is probably because the chelated Co(II) and Mn(II) complexes cannot be oxidized by the $I_2^{\cdot-}$ ion.

The effect of metal ions on the rate constants for the photo-reduction of iodine by H_3cpida is shown in Fig. 6. Neither Mg^{2+} nor Ca^{2+} ions affect the rates of the reactions for all of the *o*-, *m*-, and *p*-H_3cpida systems. On the other hand, such ions as Cu^{2+} and Zn^{2+} significantly affect the rate for only the *o*-isomer, suggesting that only the *o*-cpida^{3-} ion could form a strong chelate complex with Cu^{2+} and Zn^{2+} ions; log $K_{M(cpida)}$=10.93 (Cu^{2+}), 8.42 (Zn^{2+}), 5.06 (Ca^{2+}), and 3.91 (Mg^{2+}) for *o*-cpida^{3-}, respectively.[11]

All of the above-mentioned results show that the chelation of monoamine-*N*-polycarboxylate to metal ions inhibited the oxidation by $I_2^{\cdot-}$, due to a masking of

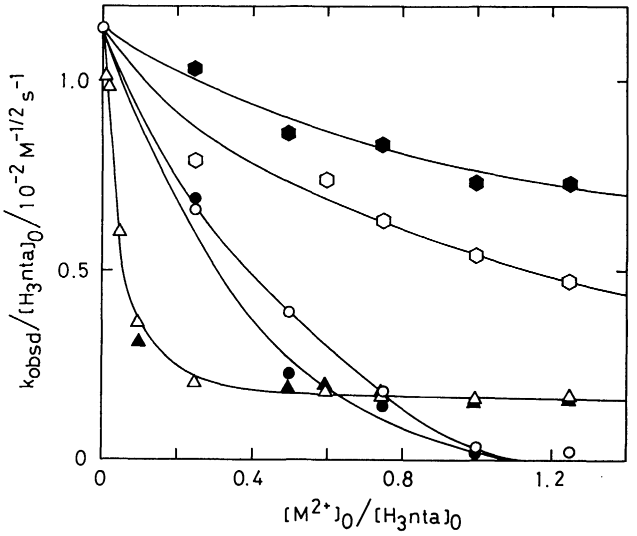


Fig. 5. Plots of $k_{obsd}/[H_3nta]_0$ vs. $[M^{2+}]_0/[h_3nta]_0$ for the photoreduction of iodine by H_3nta at pH 7.50 and $[H_3nta]_0=1.00\times10^{-4}$ M. Other conditions are the same as in Fig. 2. ○: Cu^{2+}, ●: Zn^{2+}, △: Co^{2+}, ▲: Mn^{2+}, ⬡: Ca^{2+}, and ⬢: Mg^{2+}.

Table 2. Effect of Metal Ions on the Rate Constants for the Photo-induced Reduction of Iodine by H_2hida and TEOA[a)]

$[M^{2+}]_0/[Y]_0$	$k_{obsd}/[Y]_0/10^{-4}$ $M^{-1/2}$ s^{-1}			
	Cu^{2+}	Zn^{2+}	Mn^{2+}	Co^{2+}
	Y=H_2hida			
0	4.79	4.79	4.79	4.79
0.01	3.75			
0.05	3.33			
0.10	1.94		4.10	2.48
0.25	1.92	3.56	3.68	2.08
0.50	0.74	2.20	3.94	2.04
0.75	0.58	1.74	4.03	1.92
1.00	0.26	1.81	4.03	1.71
1.25	0.21	1.74		1.67
	Y=teoa			
0	3.78	3.78	3.78	3.78
0.01	2.78			5.12
0.05	1.71			5.42
0.10	1.41	3.80		4.93
0.25	0.97	3.87	3.26	4.75
0.50	0.69	3.96	3.56	4.84
1.00	0.72	3.73	3.47	4.77
1.25				4.99

a) At 25 °C, pH 4.60 (a 0.1 M acetate buffer). I_0= 1.41×10^{-7} M s^{-1}, $[I_2]_0=1.00\times10^{-5}$ M, $[I^-]_0=1.00\times10^{-3}$ M, and $[Y]_0=1.00\times10^{-3}$ M.

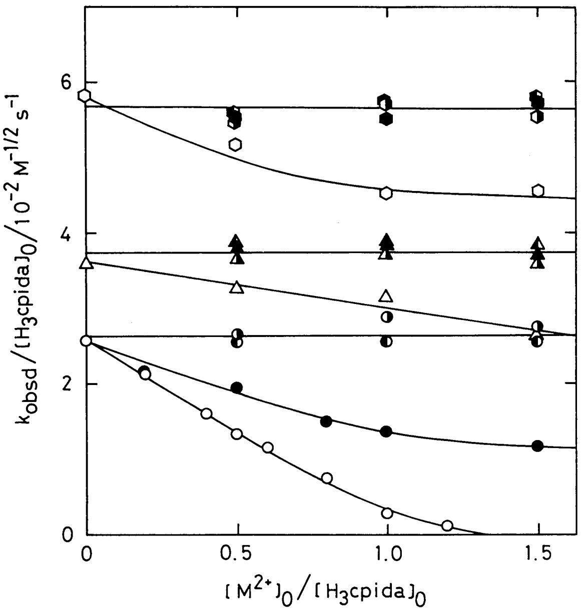


Fig. 6. Plots of $k_{obsd}/[H_3cpida]_0$ vs. $[M^{2+}]_0/[H_3cpida]_0$ for the photoreduction of iodine by H_3cpida at pH 4.60 and $[H_3cpida]_0=5.00\times10^{-5}$ M. Other conditions are the same as in Fig. 2. ○: Cu^{2+}, ●: Zn^{2+}, ◑: Ca^{2+} and ◐: Mg^{2+} for *o*-H_3cpida, ⬡: Cu^{2+}, ⬢: Zn^{2+}, ◑: Ca^{2+}, and ◐: Mg^{2+} for *m*-H_3cpida, △: Cu^{2+}, ▲: Zn^{2+}, ▲: Ca^{2+}, and ▲: Mg^{2+} for *p*-H_3cpida.

the lone electron-pair of amine nitrogen. This is consistent with the pH effect on the reaction.

This research was partly supported by a Grant-in-Aid for Scientific Research Nos. 01470051 and 03303005 from the Ministry of Education, Science and Culture.

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