Tetrahedron Vol 25, pp 4633 to 4641. Pergamon Press 1969. Printed in Great Britain.

SALT EFFECT ON METALLIC ION-CATALYSED AUTOXIDATION OF L-ASCORBIC ACID[1]

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(*Received in Japan* 9 *May* 1969; *Received in the UK for publication* 3 *June* 1969)

Abstract—Kinetics of Cu(II)-catalysed autoxidation of ascorbic acid in aqueous solutions has been studied in the presence of halides, thiocyanate and cyanide ions. The effect of these additives on the rate can be explained in terms of "ligand effect" which includes coordination ability (the order of spectrochemical series[2]), *trans* effect[3] and instability effect (or leaving ability[3]) of the anion of additive. Fast consumption of ascorbic acid even in the absence of Cu(II) occurs on addition of KNO_2 or KF. Virtually no effect is observed with KNO_3 probably because NO_3^- is a good leaving ligand and its ionic strength does not affect the autoxidation. The acceleration with KCl is maximum, when $[Cl^-]$ is nearly equal to initial concentration of ascorbic acid. Effect of oxygen pressure (p_0) on the rate in the presence of Cl^- suggests the intermediary metallic complex composed of O_2, Cl^- and ascorbate ion. Complex formation and ligand effect are further confirmed both in the autoxidation of ascorbic acid catalysed by Ni(II), Co(II) and Fe(III) and also in the autoxidations of catechol and phenol catalysed by these metallic ions.

AUTOXIDATION catalysts such as Cu, Ni, Co and Fe salts are widely used, but no convincing reason for the specific abilities and selectivities is known; their redox potentials, given in ordinary textbooks, are not always the satisfactory measure. Another interesting and important feature in the autoxidation is the acceleration and retardation affected by some other ions such as halide ion. An example is the Cu(II)-catalysed autoxidation of ascorbic acid in the presence of other additives, where the retardation mechanism may be classified into two types; (i) Chelating agents such as EDTA and metaphosphate form with Cu(II) stable complexes which are no longer effective catalysts. (ii) Some compounds, e.g. carbon monoxide, form stable complexes with Cu(I) which resist oxidation to Cu(II), i.e. an effective catalyst.

There may be, however, another effect which affects the redox potential of the metallic ion. We wish to call it "ligand effect", which brings about acceleration and also retardation depending on the nature and amount of added salts as has been reported with halide,[4] azide and cyanide salts.[5]

The present paper is an attempt for the elucidation of the effect of added salts in the $Cu(NO_3)_2$-catalysed autoxidation of ascorbic acid in aqueous solutions.

RESULTS AND DISCUSSION

Effect of additives on the rate. The effect of Cl^-, Br^-, I^-, SCN^- and CN^- on the rate of $Cu(NO_3)_2$-catalysed autoxidation of ascorbic acid is shown in Fig. 1. The kinetics were investigated in aqueous solutions, in order to avoid interference of buffering anions. Fig. 1 shows plots of psuedo-first-order rate constant (k) *vs* log [additives].

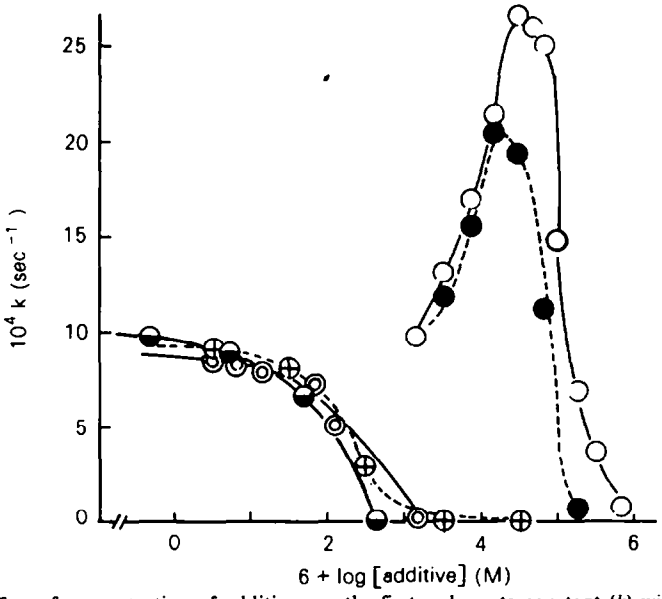


FIG. 1 Effect of concentration of additives on the first-order rate constant (k) with initial [ascorbic acid], 3×10^{-2}M; [$Cu(NO_3)_2$], 3×10^{-4}M and partial pressure of oxygen, 1 atm at 25°. —○— KCl, —●— KBr, —⊕— KI, —◎— KSCN, —⊖— CN^- from $K_3Fe(CN)_6$. k in the absence of additives was $9{\cdot}1 \times 10^{-4}$ sec^{-1}.

The figure shows Cl^- and Br^- ions have an acceleration effect, especially Cl^- accelerates the autoxidation about three fold at optimum condition. There was no effect of ionic strength for the addition of KNO_3, i.e. rate constants (10^4k sec^{-1}) at 0, 0·1 and 1·0M were 9·10, 9·07 and 9·17, respectively. Dekker *et al.*[6] reported, without describing their experimental conditions, that Cu(II)-catalysed autoxidation of ascorbic acid in HClaq proceeds 50–100 times as fast as in nitric or perchloric acid of the same concentration. The authors reexamined this effect by using HCl and HNO_3, the results are shown in Fig. 2.

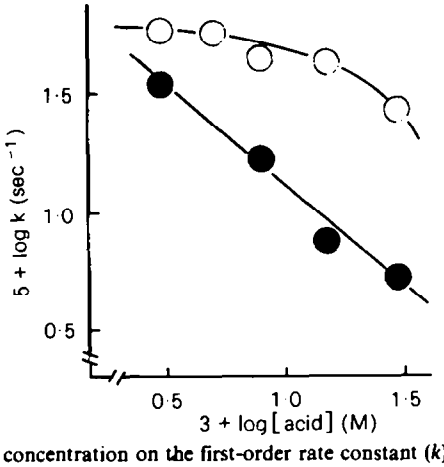


FIG. 2 Effect of acid concentration on the first-order rate constant (k) with initial [ascorbic acid], 3×10^{-2}M; [$Cu(NO_3)_2$], 3×10^{-4}M and partial pressure of oxygen, 1 atm at 25°. ● HNO_3, ○ HCl.

The feature observed on addition of HNO_3 agrees with our previous mechanism.[7] On the contrary, the rate constants show a complex variation as the concentration of HCl varies. This result may be caused by Cl^-.

The difference between the effects of Cl^- and Br^- (Fig. 1) may be ascribed to the "ligand effect" which will be mentioned in the next section. Mapson[4] has observed the acceleration with KI in an acidic buffer. Since I^- has a poor coordination ability and a high trans effect described below, the acceleration is attributable to the oxidation of ascorbic acid by molecular iodine formed.

$$2\,I^- + 2\,H^+ + \tfrac{1}{2}\,O_2 \rightarrow I_2 + H_2O \qquad (1)$$

$$I_2 + H_2A \rightarrow \underset{\text{(dehydro-ascorbic acid)}}{DA} + 2\,HI \qquad (2)$$

The hydrogen iodide produced is autoxidized to iodine again in an acidic solution.

Alternatively, I_2 may be formed by Eq. 3 which corresponds to the iodometry of cupric ion.

$$2\,Cu(II) + 4\,I^- \rightarrow 2\,CuI + I_2 \qquad (3)$$

But the formation of CuI should retard the reaction. In fact, the reaction mixture at high concentration of I^- became turbid by the formation of CuI. Thus the effect of I^- shown in Fig. 1 is explicable with ligand effect and/or an unusual reaction (Eq. 3).

It is evident[8] that thiocyanate and cyanide salts suppress the autoxidation effectively, Fig. 1 showing that both ions have almost the same inhibition effect, if their complete dissociation at low concentration occurs. It is rather strange that Butt *et al.*[5] have observed ca. 1·3 fold acceleration by using $Ca(OH)_2$–$Cu(CN)_2$ at higher pH of 5·5.

In the present experiment, potassium ferricyanide was used as a source of CN^- ion. The catalytic ability of Fe(III) is much less than that of Cu(II) and the ligand (CN^-) exchange between Fe(III) and Cu(II) should be very fast, since the colour change of the solution from slight yellow to pink red is very fast. The same CN^- effect was observed with potassium ferrocyanide (Fe(II) is a quite weak catalyst). The effect of SCN^- and CN^- on the autoxidation is also explained by the ligand effect described below.

Effect of cation of additives were examined with NaBr in the place of KBr. Virtually no effect of cation is observed as shown in Table 1.

Ligand effect. Solvent and oxygen molecules and others can coordinate competitively with metallic ion, resulting in the change of the redox potential of the metallic ion. The ligand field theory (LFT)[2,3] and crystal field theory (CFT)[2,3] may be applicable to this case and the resulting phenomena would be simply called as "ligand effect" in this paper. The effect may be composed of several factors: (i) Spectrochemical series

TABLE 1. EFFECT OF CATIONS OF ADDITIVES ON THE FIRST-ORDER RATE CONSTANT (k) AT 25°. INITIAL CONCENTRATION OF ASCORBIC ACID, $3{\cdot}0 \times 10^{-2}$M; $[Cu(NO_3)_2]$, $3{\cdot}0 \times 10^{-4}$ M; PARTIAL PRESSURE OF OXYGEN, 1 atm.

KBr(M)	10^4k (sec^{-1})	NaBr (M)	10^4k (sec^{-1})
0·003	11·7	0·003	11·8
0·03	19·3	0·03	20·3
0·3	0·68	0·3	0·68

or Fajans–Tuchida series[2] which indicates the order of separation energy (Δ) between two energy levels, e_g and t_{2g}. The series is shown in the following and is almost equal to the coordination ability with metallic ions.

$$CN^- > NO_2^- > H_2O > NO_3^- > F^- > N_3^- \sim SCN^- \sim Cl^- > Br^- > I^-$$

(ii) The *trans* effect has the following order.[3]

$$CN^- > NO_2^- \sim I^- \sim SCN^- > Br^- > Cl^- > H_2O$$

If a substrate in a metal complex is sited on the *trans* position to the ligand anion having stronger *trans* effect, the substrate is easily liberated from the central metal in the oxidation. (iii) Instability effect, which is newly proposed, implies the mobility of ligand from a complex and therefore is related to the instability constant of the complex. The order of mobility, i.e. leaving ability, is in the order:[3,9]

$$NO_3^- > H_2O > Cl^- > F^- > SCN^- > NO_2^- > CN^-$$

The order of this effect with an exception of NO_3^- is almost the reverse of the *trans* effect. (iv) The *cis* effect[3] is much less important than *trans* effect, and steric effect[3] is negligible in the case of the anions studied here.

The effect on the rate, shown in Fig. 1, may be explained in view of the ligand effect.

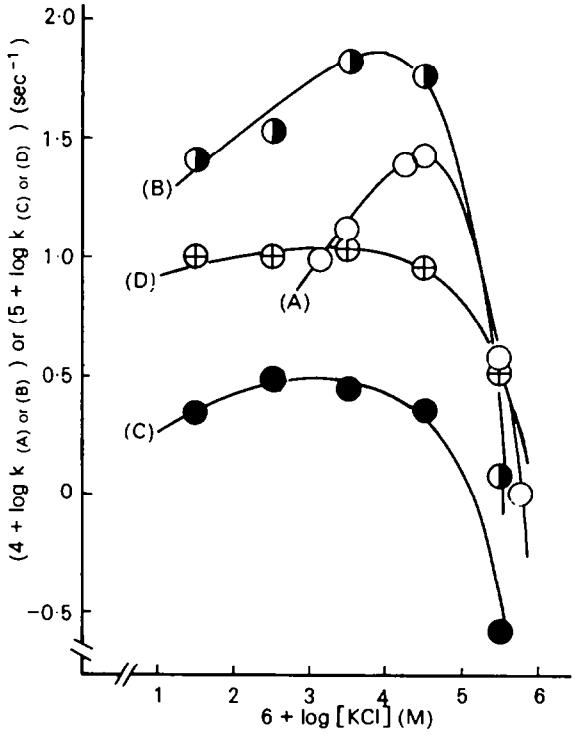


FIG. 3 Effect of ratios $[H_2A]_0$ vs. [Cu(II)] and $[H_2A]_0$ vs. $[Cl^-]$ on the first-order rate constant ($k_{(A)\sim(D)}$) with (A) $[H_2A]_0$, 3×10^{-2}M; $[Cu(NO_3)_2]$, 3×10^{-4}M; (B) $[H_2A]_0$, 3×10^{-3}M; $[Cu(NO_3)_2]$, 3×10^{-4}M; (C) $[H_2A]_0$, 3×10^{-2}M; $[Cu(NO_3)_2]$, 3×10^{-6}M; (D) $[H_2A]_0$, 3×10^{-3}M; $[Cu(NO_3)_2]$, 3×10^{-6}M at 25°. ($[H_2A]_0$: Initial concentration of ascorbic acid)

The order of spectrochemical series is $H_2O > NO_3^- > Cl^- > Br^- > I^-$, but part of the halide ions can coordinate with Cu(II), if they are in high concentration. The nitrate ion, which was used for the proof of the absence of ionic strength effect in the autoxidation, is higher in the spectrochemical series than Cl^- or Br^-, but the instability order is $NO_3^- > H_2O > Cl^- > Br^-$. Therefore, aquation predominates over the coordination of NO_3^- ion. The cyanide ion having strong spectrochemical and *trans* effects can coordinate strongly to Cu(II) and expels effectively other ligands including substrate and halide ions. The autoxidation was inhibited by addition of over 3×10^{-3}M CN^-, even when optimum condition for acceleration by 3×10^{-2}M KCl (cf. Fig. 1) was used.

Ligand effect was further examined by changing the ratios $[H_2A]_0/[Cu(II)]$ or $[H_2A]_0/[Cl^-]$ using KCl, where $[H_2A]_0$ is initial concentration of ascorbic acid (Fig. 3).

Although the acceleration is not remarkable at lower concentration of the complex, a maximum of reaction rate constant exists at almost the same ratio (ca. 1) of $[H_2A]_0/[Cl^-]$. This fact suggests that these two ligands, i.e. ascorbate monoanion and Cl^-, coordinate to Cu(II) in a certain ratio to cause favourably an electron transfer for the oxidation of ascorbate monoanion.

Unusual action of additives. An abnormal effect of additives was also observed in the following two cases. Firstly, the NO_2^- ion, which is high in the order of both spectrochemical and *trans* effects and is analogous to the CN^- ion, does not show the ligand effect, but rapid oxidation of ascorbic acid was observed even in the absence of copper catalyst. This may be ascribed to the following mechanism.

$$KNO_2 \rightleftarrows K^+ + NO_2^- \tag{4}$$

$$NO_2^- + H^+ \rightleftarrows HNO_2 \tag{5}$$

$$2\,HNO_2 \rightleftarrows NO + H_2O + NO_2 \tag{6}$$

$$NO + \tfrac{1}{2}O_2 \rightleftarrows NO_2 \tag{7}$$

$$NO_2 + H_2A \rightarrow NO + DA + H_2O \tag{8}$$[10]

Secondly, the F^- ion accelerates the autoxidation, but the rate is not first-order in ascorbic acid and the oxidation also occurs without copper catalyst. There is still no rational explanation[11] for this abnormality of the F^- ion.

Effect of partial pressure of oxygen (p_0).[12] In the Cu(II)-catalysed autoxidation of ascorbic acid, two complexes I and II should exist, since a plotted line of k *vs* p_0 does not pass through the origin and the ratio of the slope to intercept varies with temperature and solvent.[13]

$$H_2A \overset{K_9}{\rightleftarrows} HA^- + H^+ \tag{9}$$

$$HA^- + Cu(II) + O_2 \overset{K_{10}}{\rightleftarrows} \underset{(I)}{[HACu(II)O_2]^-} \tag{10}$$

$$HA^- + Cu(II) \overset{K_{11}}{\rightleftarrows} \underset{(II)}{[HACu(II)]^-} \tag{11}$$

Further support for complex II is the isolation of cuprous salt in the absence of oxygen.[14]

A similar complex III is conceivable in the presence of Cl^-.

$$HA^- + Cu(II) + m\,Cl^- \overset{K_{12}}{\rightleftarrows} [HACu(II)Cl_m]^{-n} \quad (12)$$

(III)

Assuming that the decomposition of these three complexes is rate-determining, the rate is expressed as Eq. 13, where k and K are rate and equilibrium constants of subscripted steps, respectively.

$$-d[H_2A]/dt = K_9 \frac{[Cu(II)]\,[H_2A]}{[H^+]} \times \{k_{10}K_{10}p_0 + k_{11}K_{11} + k_{12}K_{12}[Cl^-]^m\} \quad (13)$$

The effect of p_0 was examined at 25° with constant total pressure (1 atm) of oxygen and nitrogen (Fig. 4). The ratio of the slope *vs* the intercept in the plot of k *vs* p_0, $k_{10}K_{10}/\{k_{11}K_{11} + k_{12}K_{12}[Cl^-]^m\}$ at 0, 3×10^{-2} and 3×10^{-1}M KCl were 2·0[13], 4·7 and 0·13 (atm^{-1}), respectively. This rate behaviour is explicable by assuming that the

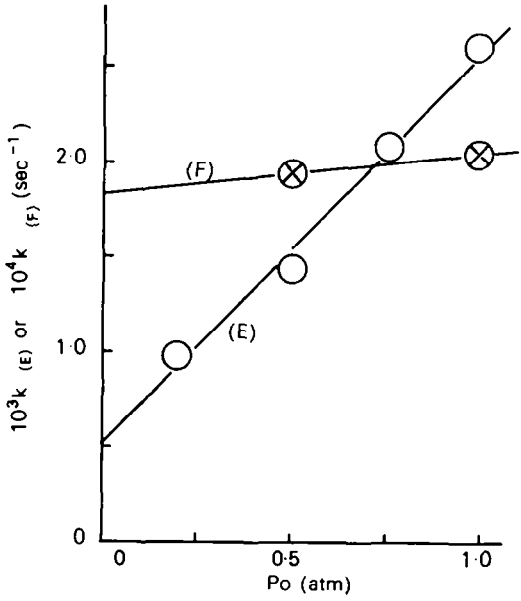


FIG. 4. Effect of partial pressure of oxygen (p_0) on the first-order rate constant ($k_{(E) \text{ or } (F)}$) with initial [ascorbic acid], 3×10^{-2}M; [$Cu(NO_3)_2$], 3×10^{-4}M at 25°. (E), [KCl] 3×10^{-2}M; (F), 3×10^{-1}M.

coordination of a little Cl^- involves the coordination of O_2 to Cu(II) and accelerates the reaction, but the coordination of a large amount of Cl^- expels O_2 and retards the reaction. Hence Eq. 14 is an expression better than Eq. 12.

$$HA^- + Cu(II) + m\,Cl^- + O_2 \overset{K_{14}}{\rightleftarrows} [HACu(II)Cl_mO_2]^{-n} \quad (14)$$

Since the ratio is small at high concentration of KCl, Eq. 15 cannot be rate-determining as reported by Mapson.[15]

$$2\,Cu(I) + 2\,H^+ + O_2 \rightarrow 2\,Cu(II) + H_2O_2 \quad (15)$$

Comparison of catalysing metallic ions. If the ligand effect is operating for the complex formation and also for the smooth oxidation of substrate with an electron transfer from the substrate towards the metallic ion, the autoxidation of ascorbic acid in the presence of other transition metals may be accelerated or retarded by addition of suitable salts. Several examples are given in Table 2. Though Ni(II), Co(II) and

TABLE 2. COMPARISON OF FIRST-ORDER RATE CONSTANTS (10^5k sec^{-1}) WITH SOME CATALYSTS IN THE PRESENCE OF KCl OF VARIOUS CONCENTRATIONS. INITIAL CONCENTRATION OF ASCORBIC ACID, 3×10^{-2}M; PARTIAL PRESSURE OF OXYGEN, 1 ATM AT 25°

Catalyst (10^{-4}M)	KCl (M)	0	3×10^{-2}	6×10^{-1}	5×10^{-6}[a]
$Cu(NO_3)_2$	3·0	91·0	266·0	9·7	89·0
$Ni(NO_3)_2$	3·0	1·9	1·9	—	—
$Ni(NO_3)_2$	30	6·0	6·4	—	—
$Co(NO_3)_2$	30	2·0	2·3	—	—
$Fe(NO_3)_3$	30	3·6	3·9	0·5	0·9

[a] $K_3Fe(CN)_6$ was added instead of KCl.

Fe(III) should form a complex similar to that of Cu(II), Ni(II) and Co(II) have poor oxidation potentials for the electron transfer from the substrate to the metal, while Fe(III) may form only a complex with a small stability constant. It is known that Cu(II) has a smaller ion radius and forms more stable complexes with many chelating agents than other transition metal ions such as Fe(III).[2a] However, even the Cu(II)-catalysed autoxidation did not show a distinct ligand effect at low concentration of Cu(II). This may be due to the very low concentration of complex formed.

Autoxidation of catechol and phenol. Our suggestion of the complex formation and ligand effect in the autoxidation of ascorbic acid was examined in the autoxidation of catechol and phenol. The results were given in Table 3.

TABLE 3. AUTOXIDATION OF CATECHOL AND PHENOL IN AQUEOUS SOLUTIONS AT 50°

Substrate (mole/10 ml)	Catalyst (10^{-3}M)		Additive (M)	Consumed O_2 (10^{-5} mole)		
				5 hr	10 hr	15 hr
Catechol	$Cu(NO_3)_2$	3·0	none	3·2	—	—
$3·0 \times 10^{-3}$	$Cu(NO_3)_2$	3·0	KCl 0·2	18·9	—	—
	$Co(NO_3)_2$	3·0	none	0	0·27	—
	none		none	0	0·20	—
Phenol	$Cu(NO_3)_2$	3·0	none	0	—	1·2
$3·0 \times 10^{-3}$	$Cu(NO_3)_2$	3·0	KCl 0·2	1·04	—	2·3

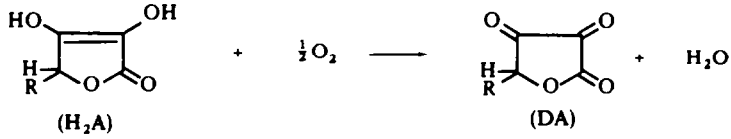
Although the stoichiometries of these reactions were not checked, the oxygen consumption at a given time increased on addition of KCl. It is known that catechol, enediol-type compound, forms a green complex with Cu(II) and a red complex with Co(II).[16] Phenol probably forms a similar complex, though its stability constant is small. This difference or the difference between bidentate anion of catechol and

monodentate anion of phenol is caused by the difference of entropy increment at the metallic complex formation. The very small dissociation degree of catechol ($K_1 = 3{\cdot}3 \times 10^{-10}$) and phenol ($K = 1{\cdot}3 \times 10^{-10}$) in an aqueous solution are not so favourable for the complex formation as ascorbic acid ($K_1 = 4 \times 10^{-5}$). In conclusion, the ligand effect of Cl^-, similar to that of ascorbic acid, is applicable to catechol and phenol which form metallic complexes.

EXPERIMENTAL

Materials. Ascorbic acid was of 99·5% pure with decomposition point of 190·9° (lit.[17] 190–192° (dec)) and optical rotation of $[\alpha]_D^{25}$ +20·94° (lit.[17] 20·5–21·5°). Catechol and phenol were commercial extra pure grade and used without further purification. Inorganic reagents were of commercial guaranteed reagent grade. O_2 and N_2 gases were of over 99·7% and 99·95% pure, respectively. Ion-exchanged water was used.

Kinetic procedure. This was the same as reported[7] and pseudo-first-order rate constant (k) was calculated by means of the usual first-order rate equation. The stoichiometry in general was as follows:



(H_2A) (DA) (16)

where R = —$CH(OH)CH_2OH$.

Alternatively, the stoichiometry of Eq. 17 may be applied.

$$H_2A + O_2 \rightarrow DA + H_2O_2 \tag{17}$$

Although most kinetical studies have estimated [H_2A] by indophenol method or [DA] by hydrazone method, the present experiments, were measured [H_2A] by UV spectrophotometry.[18] It was observed that Eq. 16 is not applicable at conversion above ca. 50% or for a rapid reaction in the presence of a considerable amount of Cu(II) or in an alkaline solution. The formed H_2O_2 reacts with ascorbic acid at lower conversion at least up to 30% and hence the stoichiometry of Eq. 16 is operating. A certain amount of H_2O_2 is consumed with ascorbic acid independent of H_2O_2 concentration.[19] The UV method[18] was advantageous not only for the proof of the H_2O_2 problem but also for the kinetics at very low concentration and of very slow reaction where the manometric method was unsuitable.

Acknowledgement—The authors would like to thank Takeda Pharmaceutical Chemical Ind. Co. for their gift of ascorbic acid.

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