# Alkali-induced Decomposition of Hydrogen Peroxide

Zoltán M. Galbács and László J. Csányi *
Institute of Inorganic and Analytical Chemistry, A. József University, P.O. Box 440, 6701 Szeged,
Hungary

It has been shown that iron(III), copper(II), and manganese(II), common contaminants of alkali-metal hydroxides, not only enhance the rate of alkali-induced decomposition of hydrogen peroxide, but also result in the rate maximum being observed at a different pH value of 11.6, 12.0, and 9.5, respectively. Different methods are recommended for the production of high-purity alkali solution and removal of contaminants. The addition of ethylenediaminetetra-acetic acid (H_4edta) to the reaction mixture resulted in a further decrease in the decomposition rate and three stages could be distinguished in the rate vs. time curves. The lowest rate (stage II) is proportional to the square of the hydrogen peroxide concentration and to the hydroxide-ion concentration. During this stage, formation of hydroxyl and superoxide radicals was observed. It is believed that the true rate of the alkali-induced decomposition of hydrogen peroxide can be determined if purified alkali and chelating agent are simultaneously employed: the rate coefficient is 3×10^{-6} dm^3 mol^{-1} s^{-1} at pH 11.6, 10^{-3} mol dm^{-3} H_4edta, and 0.1 mol dm^{-3} H_2O_2 at 308 K.

Hydrogen peroxide, an intermediate in $O_2 \rightleftharpoons H_2O$ redox transitions, is a thermodynamically unstable compound, the free enthalpy change of reaction (i) being -210.71 kJ.[1]

$$2 \ H_2O_2(aq) \longrightarrow 2 \ H_2O + O_2 \qquad (i)$$
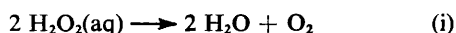
When disproportionation occurs, therefore, hydrogen peroxide species (H_2O_2 and HO_2^-) must be present which act as oxidant and reductant. This is the reason why hydrogen peroxide decomposes more quickly in alkaline solution than in neutral or acidic media.

Many efforts have been made to clarify the autodecomposition of hydrogen peroxide, but these have not yet led to a satisfactory answer because of contradictions concerning the homogeneous or heterogeneous [2-10] character of the decomposition, its pH dependence [7-16] and kinetics,[7-11,15,16] the rate-influencing effects of possible impurities, and the mechanism [7,12] of the reaction.

In the present article we report the results of experimental work in which we sought further to elucidate these questions.

Experimental

Materials.—The hydrogen peroxide used was a Merck product (Perhydrol) not containing stabilizers. The other chemicals were of reagent quality. The water used to prepare solutions was purified in several stages.[17]

Sodium hydroxide solutions were prepared in various ways. (1) Reagent quality NaOH was dissolved in distilled water, and used without special purification. (2) A solution obtained as in (1) was purified either with magnesium hydroxide [18] or with phenyl 2-pyridyl ketone oxime [9,19] and stored in polyethylene vessels. (3) By the reaction of metallic sodium or sodium amalgam with water. (4) A repeatedly recrystallized sodium sulphate solution was electrolysed with a graphite anode and a platinum cathode in a Pyrex cell separated into compartments with a G4 sinter plate, and the solution from the cathode compartment was used as the alkaline solution. (5) By the dissolution of sodium peroxide or sodium hydrogenperoxide in water. The hydrogenperoxide was prepared as follows. Merck Perhydrol was added in portions to a 10 mol dm^{-3} sodium hydroxide solution previously purified with magnesium hydroxide. It was assumed that the initially deposited white sodium hydrogenperoxide coprecipitates most of the remaining heavy-metal impurities in the form of oxides or peroxides, and this deposit was discarded. The sodium hydrogenperoxide which precipitated last, and which was considered to be the purest, was used for the kinetic measurements.

Apparatus.—The reaction vessel was a ground-glass stoppered test-tube or flask (25 or 100 cm^3). Such vessels and the glass utensils were degreased with permanganic acid, washed well with tap-water, and then left to stand for a long period in contact with a mixture of nitric acid and hydrogen peroxide. Finally, they were rinsed repeatedly with distilled water.

The temperature was maintained at a value constant to ± 0.05 K. Spectrophotometric measurements were made with Unicam SP 800 and Spekol instruments. A Radiometer TTT 1 C titrator was used for pH measurement and as a pH-stat. The e.s.r. measurements were performed with a JEOL-JES-PE spectrometer at the temperature of liquid nitrogen.

Measurements.—Hydrogen peroxide concentrations were determined titrimetrically. Accurately measured samples (1—5 cm^3) from portions of reaction mixtures were added to arsenic(III) acid of exactly known concentration. The excess of arsenic(III) was back-titrated with standard cerium(IV) sulphate solution, using ferroin as indicator and OsO_4 as catalyst.

The pH of reaction mixtures was determined at the beginning and at the end of the reaction, using appropriate portions of the mixture. The pH change did not exceed 0.1 unit.

The concentration of the superoxide radical was determined by e.s.r. measurements on samples taken from the reaction mixture and frozen with liquid nitrogen.

For the kinetic measurements, known quantities of water, sodium hydroxide, and additive (aminopolycarboxylates, metal-ion solutions, etc.) were mixed in a Pyrex vessel and thermostatted for 30 min. The reaction was then initiated by the addition of concentrated (1—10 mol dm^{-3}) hydrogen peroxide solution; the initial pH and hydrogen peroxide concentration were measured.

Results

Nature of Vessels.—When unpurified alkali was used, the same decomposition rate was observed in most vessels made of Ergon, Ersza, Duran, and Pyrex glass. When purified alkali was used, more appreciable differences emerged, depending on the nature of the vessels. The lowest amount of decomposition,

Table. Specifications of reagents according to their producers

| Impurity | Amount (μg g^{-1}) of impurity in: | | | | | | Calculated concentration of the given ion in reaction mixture (mol dm^{-3}) [a] |
	KOH (BDH)	KOH (Merck)	NaOH (Merck)	H$_2$O$_2$ (Merck)	MgSO$_4$ (Merck)	H$_4$edta (Merck)	
Fe	2	5	5	0.1	1	5	2.1 × 10^{-7}
Cu	0.5		0.5	0.01	5	1	1.8 × 10^{-8}
Mn	0.05	0.5	0.5		5		1.8 × 10^{-8}
Ni	1	1	1	0.01			3.6 × 10^{-8}
Ag	0.05						
Heavy metals [b]		5			5	5	

[a] The reaction mixture (made from Merck chemicals without purification) contains 1 mol dm^{-3} H$_2$O$_2$, at pH 11.6. [b] Those precipitable with hydrogen sulphide.

and reproducible results, were obtained in reaction vessels made of Pyrex glass or silica. Siliconizing the reaction vessels with dichlorodimethylsilane dissolved in carbon tetrachloride did not result in a significant change in the decomposition rate, neither did coating the reaction vessels with paraffin.

Purity of Chemicals.—The Table lists the producer's analysis data for the chemicals used in this study. These reveal that most of the impurities are present in the alkali-metal hydroxide preparations. The chemicals contain numerous heavy-metal impurities, among them iron, copper, and manganese ions, in relatively high concentrations. Their presence in the sodium hydroxide and magnesium sulphate preparations used here was detected by emission spectrography.

The decomposition rate of H$_2$O$_2$ could be decreased if heavy-metal hydroxides were first removed by coprecipitation with magnesium hydroxide according to D'Ans and Mattner.[18] This method was found to be even more effective if the magnesium hydroxide was precipitated in the reaction mixture itself, the metal contaminants of all the components (NaOH, water, H$_2$O$_2$) of the reaction mixture thereby being collected.

Purification by complexing with phenyl 2-pyridyl ketone oxime[9] was also found to be efficient (Figure 1).

Joint purification of the sodium hydroxide solution and the hydrogen peroxide by means of sodium hydrogenperoxide formation was found to be the most effective (Figure 1).

The other methods used to prepare the sodium hydroxide solution (dissolution of sodium, electrolysis of sodium sulphate solution) proved to be less effective and resulted in too high a decomposition rate.

pH Dependence of Decomposition.—A study of the pH dependence revealed that in most alkaline solutions a maximum in decomposition rate occurred in the interval pH 11—12. The pH dependences of the decomposition rates measured with unpurified and with purified alkali were similar in character: purification led to a decrease in the decomposition rate, but the pH of the maximum remained approximately the same (Figure 1).

Specific Effects of Metal-ion Contaminants.—In order to establish the effects of the heavy-metal impurities, different metal salt solutions were systematically added to the reaction mixtures consisting of purified reagents, and studies were made of the pH dependence of the decomposition and also of the order with respect to the hydrogen peroxide concentration.

On the addition of iron(III) the position of the maximum in the plot of decomposition rate *vs.* pH was practically unchanged, but the rate increased in proportion to the added iron(III) concentration. On the addition of copper(II) or of manganese(II), the maximum in decomposition rate was
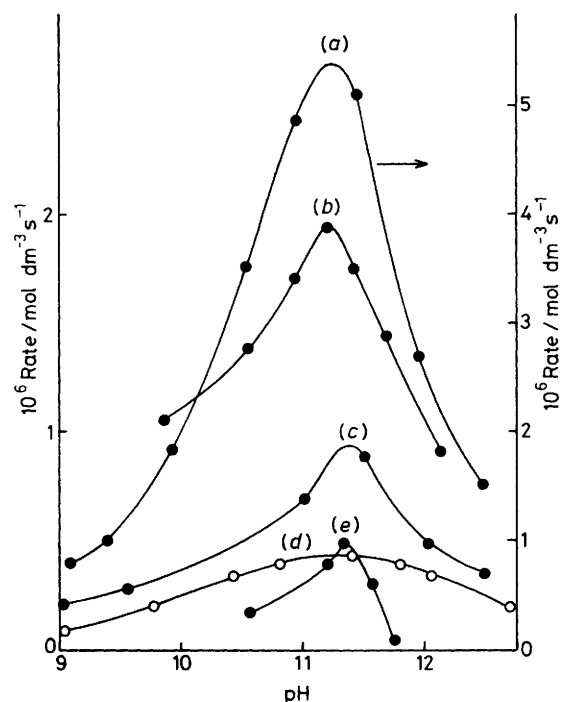

Figure 1. pH Dependence of the rate of decomposition of hydrogen peroxide. Conditions: 0.1 mol dm^{-3} H$_2$O$_2$, 308 K. Alkali solution used to adjust pH: (a) unpurified NaOH; (b) NaOH prepared by electrolysis of Na$_2$SO$_4$ solution; (c) NaOH purified with phenyl 2-pyridyl ketone oxime; (d) NaOH prepared by hydrolysis of NaHO$_2$. Curve (e) shows the pH dependence of the initial rate according to data from Figure 2 of ref. 9

observed at pH 12 or 9.5, respectively (Figure 2). In the presence of osmium,[17] ruthenium, platinum, molybdenum, tungsten, and nickel the maximum occurred at pH 10.5—10.7.

Dependence of Decomposition on H$_2$O$_2$ Concentration.—Plots of log rate *vs.* log [H$_2$O$_2$] indicated that the decomposition rates at pH 11.2 and 12.5 were proportional to the square of the hydrogen peroxide concentration, while that at pH 10 was proportional to [H$_2$O$_2$]$^{1.8}$ [Figure 3(d)—(f)]. In the presence of iron(III) or copper(II) the rate of decomposition remains porportional to [H$_2$O$_2$]^2, but in the case of manganese(II) the order lies close to 1 [Figure 3(a)—(c)].

Elimination of Effects of Metal Contaminants with Aminopolycarboxylates.—Aminopolycarboxylates were used to mask
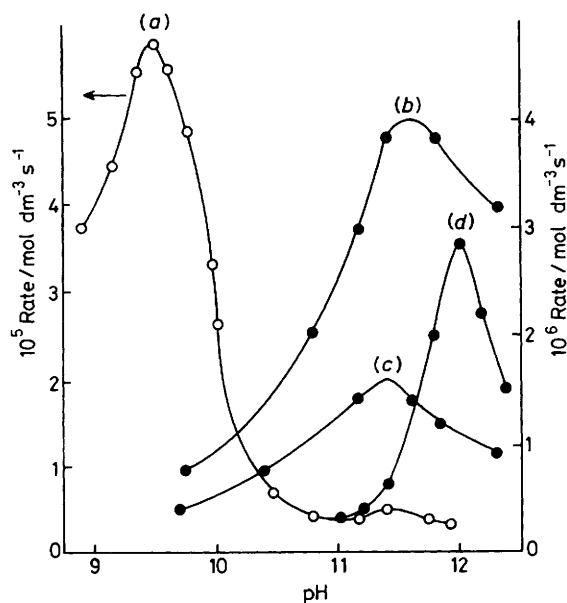
Figure 2. pH Dependence of the rate of decomposition of hydrogen peroxide in the presence of various metal ions. Conditions: 0.1 mol dm^{-3} H$_2$O$_2$, 298 K, purified NaOH.[18] Additives: (a) 5 × 10^{-5} mol dm^{-3} MnSO$_4$; (b) 10^{-5} mol dm^{-3} Fe$_2$(SO$_4$)$_3$; (c) 1 × 10^{-6} mol dm^{-3} Fe$_2$(SO$_4$)$_3$; (d) 1 × 10^{-6} mol dm^{-3} CuSO$_4$
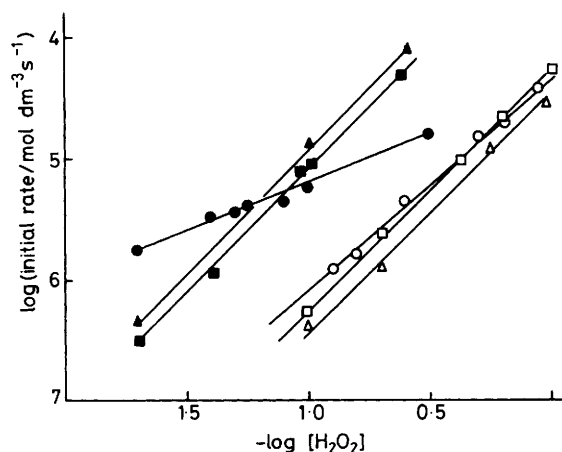

Figure 3. Logarithm of the initial decomposition rate as a function of the logarithm of initial hydrogen peroxide concentration. Conditions: (●) pH = 9.5, 298 K, 10^{-5} mol dm^{-3} MnSO$_4$; (▲) pH = 11.9, 308 K, 5 × 10^{-8} mol dm^{-3} CuSO$_4$; (■) pH = 10.9, 308 K, 10^{-6} mol dm^{-3} Fe$_2$(SO$_4$)$_3$; (○) pH = 10.0, 308 K; (□) pH = 11.2, 308 K; (△) pH = 12.5, 298 K

the heavy-metal impurities and to diminish their catalytic effects. When the variation in the hydrogen peroxide concentration as a function of time is measured in the presence of H$_4$edta (ethylenediaminetetra-acetic acid, as its disodium salt), H$_5$dtpa (diethylenetriaminepenta-acetic acid), H$_4$dodta (3,6-dioxaoctane-1,8-diaminetetra-acetic acid), H$_3$nta (nitrilotriacetic acid), or H$_4$cdta (cyclohexane-1,2-diaminetetra-acetic acid), most of the curves consist of three stages. Initially, the concentration change is practically the same as in the absence of these chelating agents (stage I). After a time, the rate decreases considerably (stage II), and finally the decomposition again increases (stage III). At a given metal-ion con-
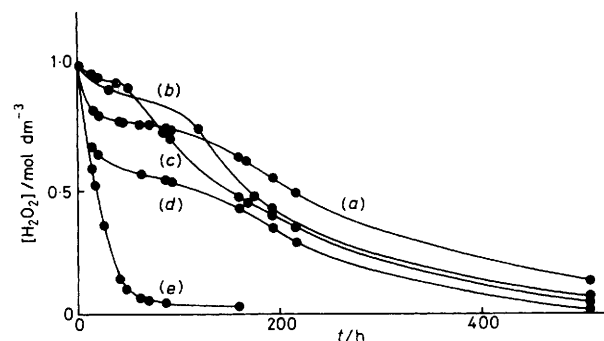

Figure 4. Decomposition of hydrogen peroxide in the presence of aminopolycarboxylates. Conditions: initial pH 11.2 adjusted with purified [18] NaOH, 298 K; (a) 2 × 10^{-3} mol dm^{-3} H$_4$edta; (b) 2 × 10^{-3} mol dm^{-3} H$_5$dtpa; (c) 2 × 10^{-3} mol dm^{-3} H$_4$dodta; (d) 2 × 10^{-3} mol dm^{-3} H$_3$nta; (e) 2 × 10^{-3} mol dm^{-3} H$_4$cdta

tent the individual stages depend on the nature of the aminopolycarboxylate (Figure 4), on its concentration, and on the pH of the solution. For instance, for H$_4$edta, stage I is shorter and stage II longer, the lower is the metal-ion concentration, the higher the H$_4$edta concentration, and the lower the pH of the solution.

When the decomposition in the presence of H$_4$edta had reached stage III, the rate could be decreased by repeated addition of H$_4$edta. As before, this decrease did not occur immediately, but after a new stage I. It should be added that, in the presence of H$_4$edta (in stage II), the rate increased monotonously with increasing pH.

Detection of Radicals.—The superoxide (hyperoxide, O$_2^-$) radical formed during the decomposition of hydrogen peroxide in alkaline media was detected by e.s.r. spectroscopy ($g_\perp$ = 2.001, $g_\parallel$ = 2.087).[20] After a reaction time of 300 s at pH 10.5, about 10^{-6} mol dm^{-3} superoxide radical could be found in a 1 mol dm^{-3} hydrogen peroxide solution made alkaline with purified sodium hydroxide. The radical concentration increased considerably on elevation of the pH or on the addition of iron(III).

The OH radical was detected by measurement of the decolouration of NN-dimethyl-p-nitrosoaniline (RNO).[21] In 0.05 mol dm^{-3} hydrogen peroxide solution made alkaline with purified sodium hydroxide, at pH 11.3 the stationary-state OH concentration [17] was found to be 1 × 10^{-17}—1.5 × 10^{-17} mol dm^{-3}.

The stationary-state concentration of the OH radical in the presence of H$_4$edta varies with time. Initially, the concentration is relatively high and progressively decreases (stage I of the [H$_2$O$_2$] vs. time curves); the lowest value arises when the rate of hydrogen peroxide decomposition too is its lowest (in stage II). When the decomposition-diminishing effect of H$_4$edta ceases (in stage III), the OH concentration again increases.

Discussion

Numerous observations [2-7] have shown that solid surfaces, among them glass of different compositions, strongly influence the rate of decomposition of hydrogen peroxide. Our experiments led to the conclusion that a glass surface acts primarily as a source of leachable impurities and has only a secondary influence on the rate as a heterogeneous catalyst. When suitably cleaned Pyrex or silica reaction vessels were

used, the surface provided a negligible source of contamination in comparison with the reagent solution. The decomposition rate could be suppressed by a factor of 15—20 when H₄edta was added to the reaction mixture. This suggests that there is no (or only a very small) surface component of the decomposition, or that aminopolycarboxylate not only behaves as a homogeneous sequestering agent but is also able to deactivate the catalytically active metallic centres on the glass surface by chelation. The fact that the decomposition rate was hardly influenced when the reaction vessel had been siliconized or coated with paraffin is similarly indicative of the non-occurrence of surface catalysis.

The chemicals used, and in particular the sodium hydroxide, proved to be major sources of contamination. The contradictory observations to be found in the literature may be interpreted in terms of the presence of impurities. As was shown by Figures 1 and 2, different positions of the maxima in the decomposition rate and different dependences on the hydrogen peroxide concentration as well as on pH could be found, depending on which metal ion was the predominant impurity, e.g. $pH_{max.} = 9.5$ for manganese, 12 for copper, and 10.5—10.7 for osmium,[17] ruthenium, molybdenum, and tungsten. Earlier investigations which demonstrated second-order kinetics and a rate maximum at pH 11—12 were connected with different rate constants and probably with systems contaminated to various extents with iron(III) ions. In the simultaneous presence of several impurities, the dependence of decomposition rate on pH may be of the maximum–minimum–maximum type,[13] as we demonstrated for a reaction mixture containing both iron(III) and manganese(II) (Figure 2).

It is difficult to remove the last traces of heavy-metal ions from concentrated alkali solution, since the large excess of hydroxide ions promote the formation of polynuclear hydroxides. Besides, the methods which may be considered for removal of impurities involve equilibrium processes (ion exchange, adsorption, extraction, etc.) and the reagents used for the purification may themselves sometimes contaminate the alkali solution (e.g. in the purification with phenyl 2-pyridyl ketone oxime[9] some of the reagent and the alcohol used for the extraction remain behind in the alkali). Thus, there are finite limits [22–25] to the purifications. It follows from the above that the lowest rate value reported in the literature and measured here by using the purest alkali (from NaHO₂) can still not be regarded as the true value for the autodecomposition of hydrogen peroxide.

If the metal-ion impurities are complexed with H₄edta and other aminopolycarboxylates, simple or mixed (OH⁻) ligand complexes are formed [26–28] and the rate of hydrogen peroxide decomposition decreases to different extents (Figure 4). The transformation of metal hydroxides, and particularly polynuclear oxide-hydroxides, to aminopolycarboxylate complexes is not instantaneous, but takes place gradually. This explains the almost unchanged fast decompositon stage (stage I) observed at the beginning of the $[H_2O_2]$ vs. time curves [following the addition of complexing agent (Figure 4)]. Obviously, the occurrence of complex formation will depend on the nature and concentration of the aminopolycarboxylate, on the concentrations of the metal ions to be masked, and on the pH.[29,30] This explains why various authors reached different conclusions when using H₄edta. For example, in measurements where much metal contamination presumably remained in the sodium hydroxide solution despite the purification [e.g. in the purification by coprecipitation of $Fe(OH)_3$[8]], the slowness of the complexation by H₄etda means that initially the decrease in decomposition rate would hardly be observable compared to the high initial rate. This could have led to the conclusion that H₄edta does not influence hydrogen peroxide decomposition.[8]

In those measurements in which the H₄edta inhibition could be observed immediately,[9] presumably because of the nature of the metal ions and their low concentration (low degree of aggregation) and also because the alkali contained residual phenyl 2-pyridyl ketone oxime, which as an auxiliary complex-former inhibited the formation of polynuclear metal hydroxides, the sequestering equilibrium with H₄edta could be established quickly, and stage I did not occur.

Although some authors [10] did observe the effect of H₄edta in reducing the decomposition rate, they followed the decomposition for only a short time and accordingly did not see the later increase of the decomposition rate (stage III) which we found.

In stage II the rate of decomposition strongly depends on the OH⁻ concentration. The masking effect of aminopolycarboxylate is lessened by increasing pH for two reasons. As the pH rises, the increasing OH⁻ concentration is more effective in competing with the chelate ligand, and the metal impurities in the solution increase in proportion to the quantity of alkali added. This is why the decomposition rate in stage II increases monotonously with pH, in contrast with the dependence on pH in the absence of H₄edta which exhibits a maximum.

It should be added that H₄edta not only behaves as a sequestering agent but it also scavenges the hydroxyl radical [31] formed during the decomposition. This is the reason why H₄edta itself undergoes decomposition during the autodecomposition of hydrogen peroxide and after a time the decomposition rate of the latter increases again. The rate in stage III is somewhat higher than it was before the addition of H₄edta, which is probably connected with the fact that metal ions are released in their more active forms when H₄edta is destroyed by radicals since they were present as polynuclear oxohydroxocomplexes of lower activity before addition of H₄edta.

The observation that the rate law for decomposition of hydrogen peroxide changes in a strongly alkaline medium or more concentrated solution of substrate is connected with the higher level of impurities. Under such circumstances the very slow autodecomposition reaction will be suppressed entirely by by the much faster catalysed decomposition. At high concentrations of alkali the contaminating metal ions are present as finely dispersed colloidal species of hydroxides and oxyhydroxides and the decomposition proceeds through interaction of hydrogen peroxide with the surface of these particles as a first-order reaction without any pH maximum.[32]

Hydrogen peroxide decomposition most free from the disturbing effects of metal ions can be observed in stage II in the presence of H₄edta. In a well purified reaction mixture the total concentration of residual metal-ion impurities is probably in the nanomolar range. This quantity can be sequestered so effectively with 10^{-3} mol dm⁻³ H₄edta that the uncomplexed metal-ion concentration must be well below 10^{-10} mol dm⁻³. The fact that the deliberate addition of the 1 : 1 iron(III)–H₄edta complex in the concentration range 1×10^{-7}—9×10^{-6} mol dm⁻³ caused only a small increase in the decomposition rate (and no change in the OH radical yield, i.e. in RNO bleaching) proves not only the high efficiency but also the considerable capacity of the masking by H₄edta. This finding is in good accordance with previous observations that the oxidation potential [26] and the reactivity of the 1 : 1 iron(III)–H₄edta complex drop considerably when mixed-ligand complexes such as $[Fe(OH)(edta)]^{2-}$ and $[Fe(OH)_2(edta)]^{3-}$ are formed [33,34] above pH 9. On the basis of these results we are of the opinion that in the presence of sufficient H₄edta and in stage II the observed rate does not differ considerably from the true rate of alkali-induced decomposition of hydrogen peroxide. According to the present investigations, the approximate rate coefficient is 3×10^{-6} dm³ mol⁻¹ s⁻¹ at 308 K (0.1

mol dm^{-3} H$_2$O$_2$, pH 11.6, 1 × 10^{-3} mol dm^{-3} H$_4$edta) if the scavenger effect of H$_4$edta is not taken into consideration.

Another question remaining to be answered is whether the alkali-induced decomposition of hydrogen peroxide proceeds *via* a radical, a molecular, or possibly a mixed mechanism. As the experiments indicate that the formation of OH and superoxide radicals can also be detected under the purest conditions and in the presence of aminopolycarboxylates too, we tend to the opinion that the alkali-induced decomposition of hydrogen peroxide is a radical-chain reaction. The details of the mechanism will be discussed elsewhere.

References
1 W. M. Latimer, 'The Oxidation States of the Elements and their Potentials in Aqueous Solutions,' Prentice-Hall, New York, 1952, p. 39.
2 R. Livingston, *J. Phys. Chem.*, 1943, **47**, 260.
3 G. Tammann, *Z. Phys. Chem. (Leipzig)*, 1889, **4**, 441.
4 T. Kompolthy, Ph.D. Thesis, Budapest, 1938.
5 K. B. Keating and A. G. Rozner, *J. Phys. Chem.*, 1965, **69**, 3658.
6 W. C. Schumb, *Ind. Eng. Chem.*, 1949, **41**, 992.
7 L. Erdey and J. Inczédy, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 93.
8 F. R. Duke and T. W. Haas, *J. Phys. Chem.*, 1961, **65**, 304.
9 E. Koubek, M. L. Haggett, C. S. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 2263.
10 K. Tanabe and K. Arata, *Shokubai*, 1965, **7**, 462.
11 K. Kolocziejczak and A. Dorabialska, *Zesz. Nauk. Politechn. Lodz., Chem.*, 1960, **8**, 3.
12 E. Abel, *Monatsh. Chem.*, 1952, **83**, 422.
13 S. Oki and Y. Kaneko, *Shokubai*, 1964, **6**, 182.
14 P. Pierron, *C. R. Acad Sci., Ser. C*, 1946, **222**, 1107.
15 H. Ali and J. M. Saleh, *J. Indian Chem. Soc.*, 1968, **45**, 908.
16 G. M. Nabar, V. A. Shenai, and A. S. Mehta, *Indian J. Technol.*, 1966, **4**, 239.
17 L. J. Csányi, Z. M. Galbács, and L. Nagy, *J. Chem. Soc., Dalton Trans.*, 1982, 237.
18 J. D'Ans and J. Mattner, *Angew. Chem.*, 1952, **64**, 448.
19 F. Trusell and H. Diehl, *Anal. Chem.*, 1959, **31**, 1978.
20 L. Nagy, Z. M. Galbács, and L. J. Csányi, *J. Chem. Soc., Dalton Trans.*, 1982, 859.
21 I. Krajlic and C. N. Trumbore, *J. Am. Chem. Soc.*, 1965, **87**, 2547.
22 D. Reiner and D. P. Poe, *Anal. Chem.*, 1977, **49**, 889.
23 Zs. Horváth, Z. Lásztity, and O. Szakács, *Anal. Chem.*, 1981, **53**, 1149.
24 W. Hoffmeister, *Fresenius' Z. Anal. Chem.*, 1978, **290**, 289.
25 P. Benes and V. Majer, ' Trace Chemistry of Aqueous Solutions,' Academia, Prague, 1980.
26 G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, 1951, **34**, 576.
27 M. Orhanovic and R. G. Wilkins, *Croat. Chem. Acta*, 1967, **39**, 149.
28 V. Baran, *Coord. Chem. Rev.*, 1971, **6**, 65.
29 G. H. Nancollas, *Coord. Chem. Rev.*, 1970, **5**, 379.
30 J. Kragten, *Talanta*, 1977, **24**, 483.
31 Ch. Walling, M. Kurz, and H. J. Schugar, *Inorg. Chem.*, 1970, **9**, 931.
32 O. Špalek, J. Bales, and I. Paseka, *J. Chem. Soc., Faraday Trans. 1*, 1982, 2349.
33 Y. A. Ilan and G. Czapski, *Biochim. Biophys. Acta*, 1977, **498**, 386.
34 J. Butler and B. Halliwell, *Arch. Biochem. Biophys.*, 1982, **218**, 174.