

## The Cobalt Chelates of Polyaminocarboxylic Acids as Initiators in the Emulsion Polymerization of Styrene

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### Synopsis

The use of cobalt(II) complexed with various polyaminocarboxylic acids and hydrogen peroxide has been shown to be an effective initiator for the emulsion polymerization of styrene. The polyaminocarboxylic acids used were ethylenediaminetetraacetic acid (EDTA), ammonia diacetic acid (ADA), N,N'-bis(2-aminoethyl)ethylenediaminehexaacetic acid (TTHA), ammonia triacetic acid (ATA), and N'-hydroxyethylethylenediamine-N,N,N'-triacetic acid (HEEDTA). In the case of the HEEDTA system, the effect of varying the concentrations of the initiator components was examined and found to be broadly similar to that observed in other metal ion chelate-hydrogen peroxide initiators. All the systems were effective over a wide pH range (generally 3-9), and zero-order rates in the range of 30-90%/hr were observed, although there was considerable variation in detail in the manner in which the zero-order rate depended on pH. The behavior of these systems is commented upon in the light of earlier results on similar systems and of previously published redox potentials of the related cobalt(II)-cobalt(III) chelate systems.

### INTRODUCTION

Redox systems have been used as polymerization initiators for many years, a notable example being in the manufacture of styrene/butadiene rubber by emulsion polymerization. A useful review of early work is provided by Bacon,<sup>1</sup> and numerous individual reports have appeared subsequently.

The hydrogen peroxide-ferrous salt combination (Fenton's reagent) has been thoroughly investigated<sup>2</sup> but is not directly applicable to all emulsion systems, in many of which the pH of the aqueous phase is above 7. In such cases, it is necessary to complex the metal ion in order to keep it in solution, and the polymerization is initiated by the free radicals formed by reaction between the complexed metal ion and hydrogen peroxide.<sup>3</sup> Initiators using iron(II),<sup>4,5</sup> iron(III),<sup>6</sup> copper(I),<sup>7</sup> copper(II),<sup>8</sup> and chromium(II)<sup>9</sup> with hydrogen peroxide, in which the metal ion has been complexed with polyaminocarboxylic acids, have been studied.

In the present paper, a further example is considered, viz., the cobalt(II)-polyaminocarboxylic acid-hydrogen peroxide system which has been used

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to initiate the emulsion polymerization of styrene. The polyaminocarboxylic acids used were ethylenediaminetetraacetic acid (EDTA), ammonia diacetic acid (ADA), *N,N'*-bis(2-aminoethyl)ethylenediaminehexaacetic acid (TTHA), ammonia triacetic acid (ATA), and *N'*-hydroxyethyl ethylenediamine-*N,N,N'*-triacetic acid (HEEDTA).

The system using HEEDTA was studied in some detail; the effect of variation of initiator components and of change in pH on the zero-order rate of polymerization were examined. In the cases of the other initiating systems mentioned above, the effect of pH change only was studied.

## EXPERIMENTAL

### Preparation and Purification of Materials

**Styrene.** Commercial-grade styrene was washed with 2*M* sodium hydroxide solution and distilled under reduced pressure in an atmosphere of nitrogen. The pure styrene was stored at 263°K.

**Nitrogen.** The British Oxygen Company's "white spot" nitrogen was deoxygenated by passing through alkaline sodium dithionite solution and subsequently through dilute sodium hydroxide solution, dilute sulfuric acid, and deionized water.

**Cobalt(II) Polyaminocarboxylic Acids.** These complexes were prepared in solution by the addition of a 100% excess of the polyaminocarboxylic acid solution (0.2*M*) to the cobalt(II) chloride solution (0.2*M*), prepared from analytical reagent-grade material.

**Hydrogen Peroxide.** Analytical reagent-grade 100 vol hydrogen peroxide (stabilizer free), containing 30.5% w/v hydrogen peroxide, was used as a stock solution. This was diluted to 2.5 vol as required.

**Emulsifying Agent.** Reagent-grade sodium lauryl sulfate was used as a 2.5% w/v solution.

**Deionized Water.** The deionized water (conductance less than  $3 \times 10^{-9} \Omega^{-1} \text{m}^{-1}$ ) used throughout was deoxygenated by boiling for 15 min and cooling under nitrogen.

### Polymerization

The basic experimental procedure used was that described by Bond and Jones.<sup>4</sup> The apparatus consisted of a three-necked, 250 cm<sup>3</sup> round-bottom flask. The central neck was fitted with a link stirrer and guide. Through one of the side arms was fitted a tube which allowed a slow stream of nitrogen to be passed through or over the reaction mixture. An Ingold combined pH electrode was fitted through the second side arm, which also served as a nitrogen outlet. The reaction flask was immersed in a constant-temperature water bath at  $323 \pm 0.1^\circ\text{K}$ , and the emulsifier solution, 100 cm<sup>3</sup> sodium lauryl sulfate solution, was added. After bubbling nitrogen gas through the emulsifier solution for 1 hr, 50 g styrene was added dropwise from a tap funnel over 10 min, steady stirring being maintained. The pH

electrode was inserted in place of the funnel and the pH of the dispersion adjusted to the desired value by addition of hydrochloric acid or sodium hydroxide solution as appropriate. Part of the initiator system, 5 cm<sup>3</sup> of the cobalt(II) chelate solution, previously adjusted to the required pH, was added by pipette. Ten equal aliquots of hydrogen peroxide, total volume 10 cm<sup>3</sup>, were added at 1-min intervals, from a burette. Zero time for the reaction was taken as the time when exactly half of the hydrogen peroxide had been added.

The pH of the mixture was monitored throughout the polymerization process and adjustments were made, usually required only during the hydrogen peroxide addition, to maintain a constant pH. Samples of the mixture were withdrawn at intervals and the percentage conversion of monomer to polymer was determined by the weight conversion method.<sup>10</sup>

In each case, percentage conversion was plotted versus time and the zero-order rate calculated as the gradient of the straight portion.

## RESULTS AND DISCUSSION

The variation of zero-order rate of polymerization ( $R_p$ ) with hydrogen peroxide concentration was studied in the case of the cobalt-HEEDTA system only. The results (Fig. 1) are presented as a plot of  $\log R_p$  versus  $\log$  peroxide concentration, and the straight line, drawn through the points by the least-squares method, has a gradient of 0.35. This is somewhat below the value of 0.4 predicted by the theories of Smith and Ewart<sup>11</sup> and Gardon.<sup>12</sup> In this respect, the present system contrasts with the ferrous chelate-hydrogen peroxide system, for which the initiator concentration dependence index was close to 0.5.<sup>4</sup>

The dependence of zero-order rate of polymerization on the concentration of the cobalt-HEEDTA complex (Fig. 2) is not in accordance with theory but is, however, in agreement with the behavior<sup>4</sup> of other, similar, metal ion chelate-hydrogen peroxide systems. The leveling off of rate of polymerization at high concentrations has been generally attributed<sup>4</sup> to mutual annihilation of radicals as a result of the high radical concentrations produced under these conditions of high catalyst activity.

The effect of pH on the zero-order rate of polymerization for this system is discussed below in conjunction with the results for the other complexing agents.

The initiation of the polymerization of styrene by the cobalt complex-hydrogen peroxide system probably proceeds by a free-radical mechanism, involving hydroxyl radicals in the oxidation of the Co(II) chelate by the hydrogen peroxide. Direct participation by Co<sup>2+</sup> and Co<sup>3+</sup> ions is unlikely in view of the extremely high stabilities of the complexes concerned (the stability constant of the least stable complex, Co(II)-ADA, is  $\approx 10^7$ ).<sup>13</sup>

The redox potential of the Co(III)-Co(II) complex system is a measure of the tendency of the lower valency state to be oxidized, and it might therefore be expected to give an indication of the effectiveness as an initiator

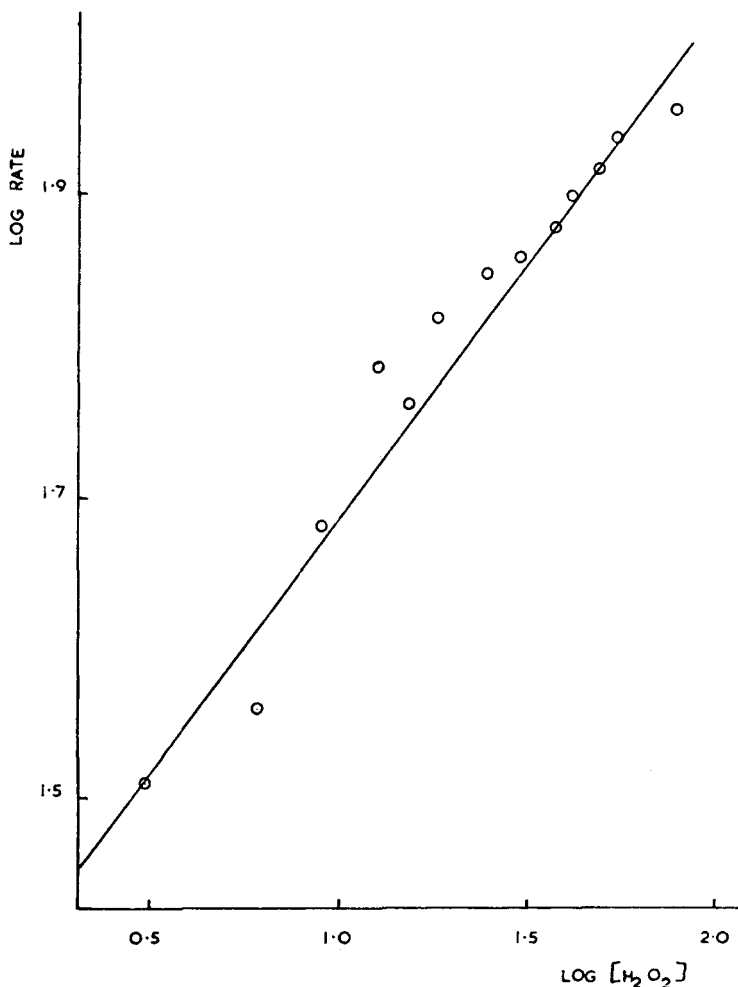


Fig. 1. Dependence of the zero-order rate of polymerization on hydrogen peroxide concentration at pH 3.5 for the cobalt(II)-HEEDTA system, as log-log plot.

of the redox system when used in conjunction with hydrogen peroxide. The redox potentials (measured with a reproducibility better than  $\pm 2$  mV)<sup>13</sup> have been found to vary considerably with pH, and it is thus to be anticipated that the zero-order rate of polymerization will also vary considerably with pH. There is also the possibility that pH may exert an influence on the rate of polymerization via an effect on the emulsifier. Little work has been reported on the influence of pH on micelle formation in sodium lauryl sulfate (and similar emulsifiers), but it has been assumed<sup>14</sup> that, since lauryl sulfuric acid and its sodium salt have the same critical micelle concentration, the latter is independent of pH. The substantial independence of rate of polymerization on pH, when using sodium lauryl sulfate in the emulsion polymerization of styrene, has been established<sup>15</sup> in a study involving an initiator (potassium persulfate) whose rate of

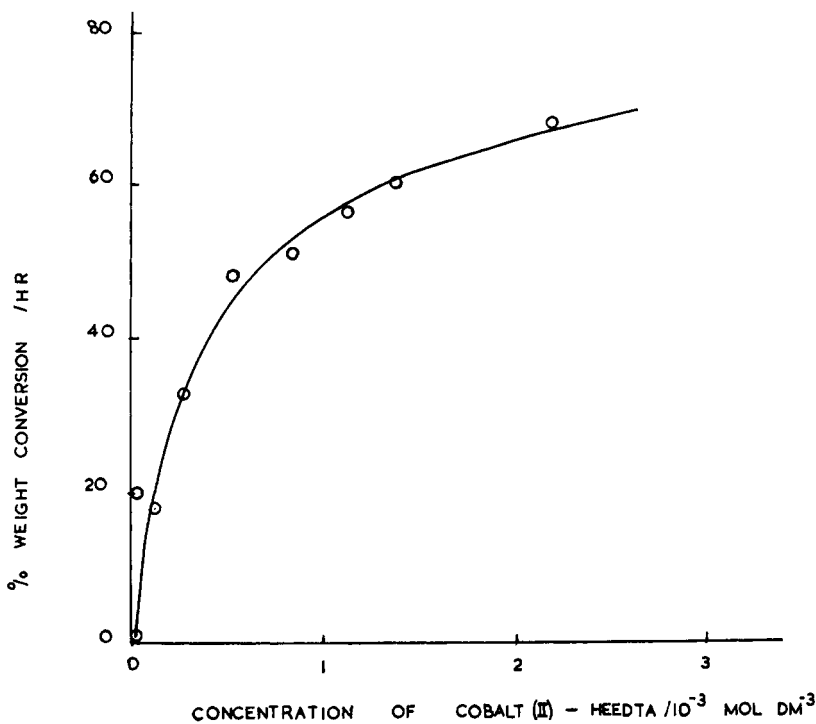


Fig. 2. Variation of zero-order rate of polymerization with concentration of cobalt(II)-HEEDTA at pH 4.

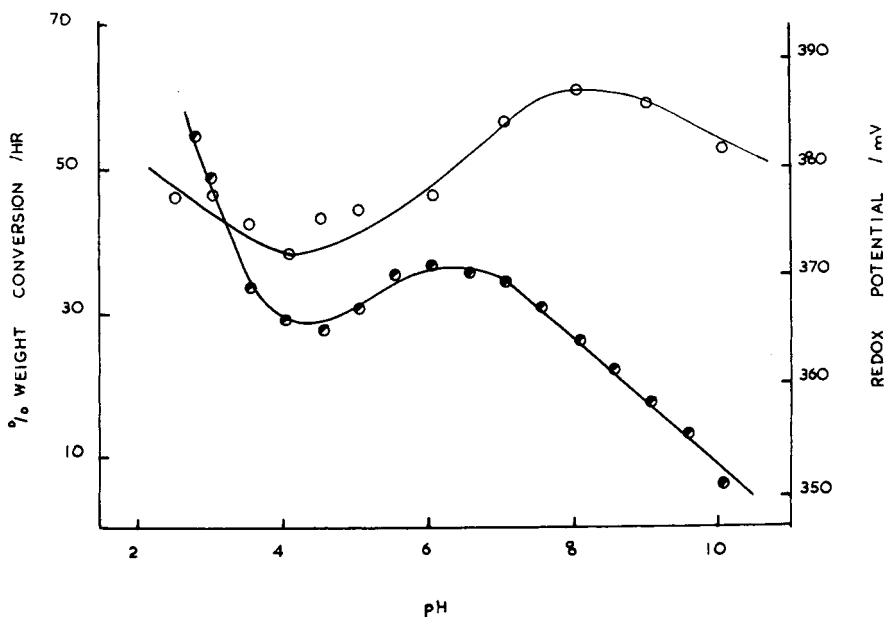


Fig. 3. Variation of zero-order rate of polymerization (O) and of redox potential (●) with pH, at constant cobalt(II)-EDTA concentration.

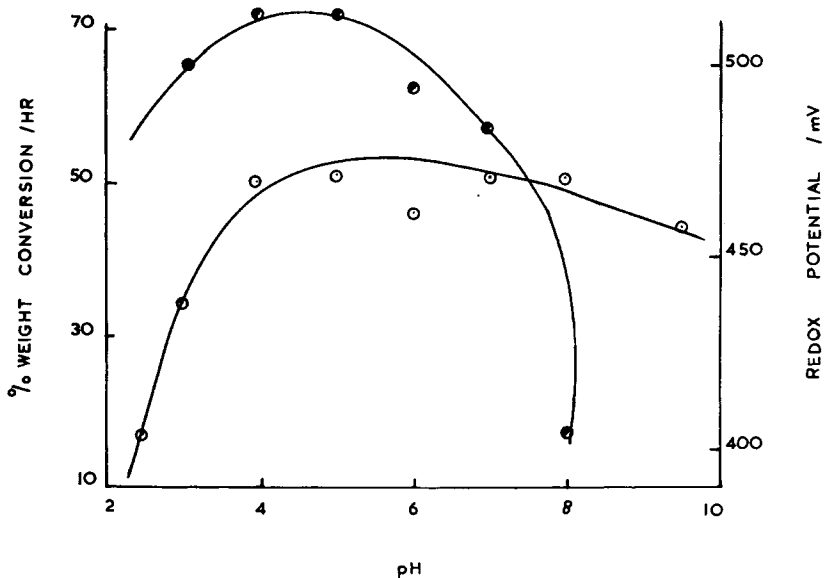


Fig. 4. Variation of zero-order rate of polymerization (O) and of redox potential (●) with pH at constant cobalt(II)-ATA concentration.

decomposition as a function of pH is known.<sup>16</sup> This work has shown that there is a slight fall in rate of polymerization from pH 7 down to pH 3, with a somewhat steeper fall below pH 3. The effect of this variation on the polymerization curves in Figures 3-7 will be slight and has been ignored.

Figures 3-7 illustrate the relationship between both redox potential and zero-order rate of polymerization and pH for each of the five systems studied. In no case did the comparable Co(III) complex bring about polymerization in a similar period of time. It is readily apparent that there is no general pattern for the series. In the case of Figures 3 and 4, the rates of polymerization and redox potentials vary with pH in a broadly similar manner. The same is also true of Figure 5, except in the region above pH 7.5. The divergence above this pH may be associated with the observation<sup>17</sup> that the cobalt-HEEDTA complex undergoes a change in structure in the region of pH 7 (from quinquedentate to sexidentate). A similar parallelism has previously been reported<sup>9</sup> for certain chromium(II)-polyaminocarboxylic acid-hydrogen peroxide systems. In this work, three complexing agents were used, one of which was EDTA.

The results illustrated in Figures 6 and 7 are in marked contrast to the previous ones. In these cases, increase of pH results in opposite changes in rate of polymerization and redox potential.

The results reported provide some support for the idea that initiator effectiveness in systems of this kind should be related to the appropriate redox potential at the relevant pH. However, many factors influence the rate of polymerization, and a simple correlation is perhaps not to be

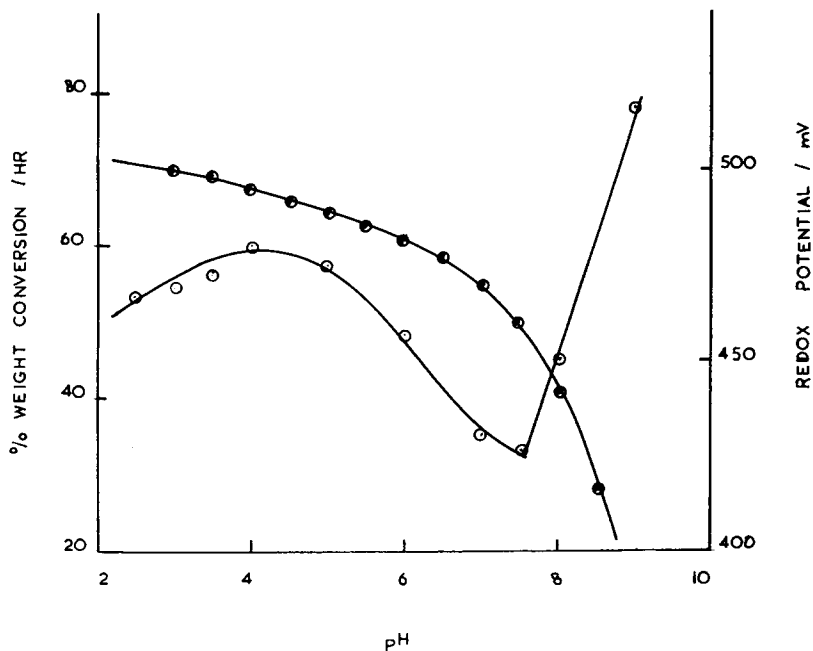


Fig. 5. Variation of zero-order rate of polymerization (O) and of redox potential (●) with pH at constant cobalt(II)-HEEDTA concentration.

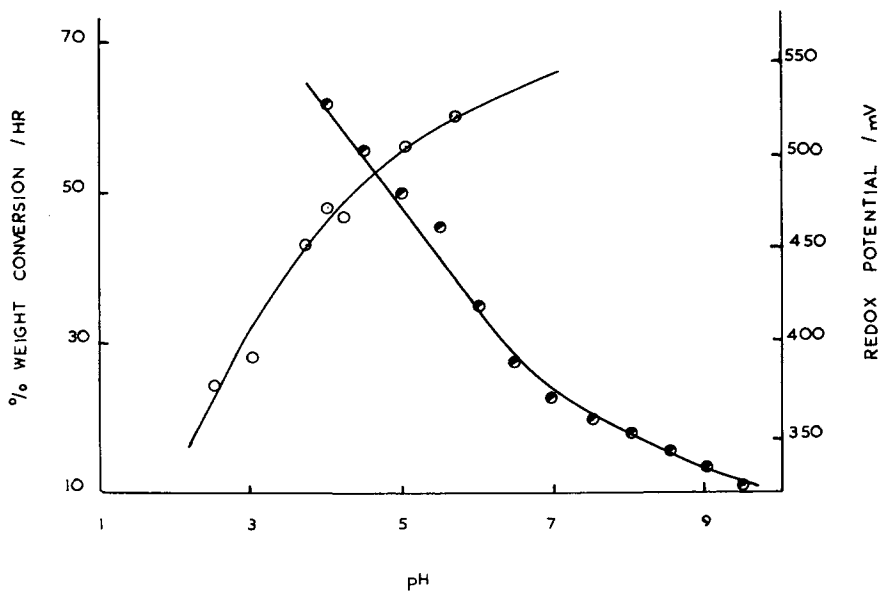


Fig. 6. Variation of zero-order rate of polymerization (O) and of redox potential (●) with pH at constant cobalt(II)-ADA concentration.

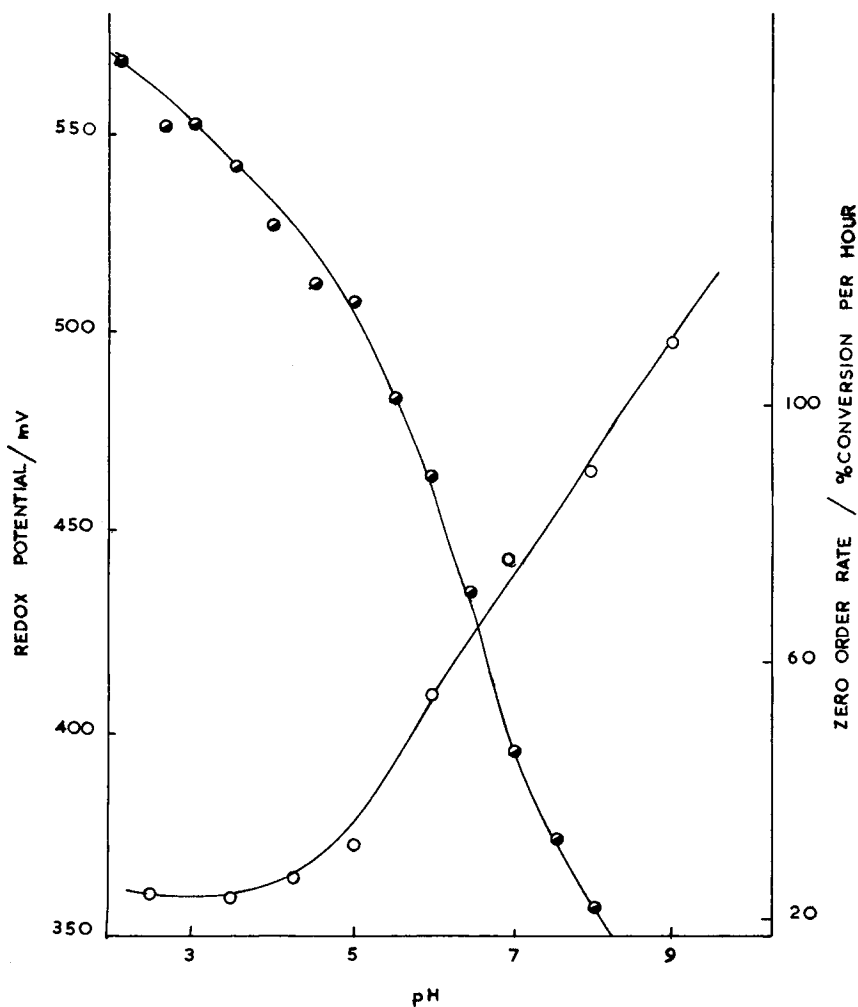


Fig. 7. Variation of zero-order rate of polymerization (O) of redox potential (●) with pH at constant cobalt(II)-TTHA concentration.

expected. In addition to redox potential, kinetic factors are likely to be important. Nothing is known of the mechanism of peroxide decomposition by these chelates, but it is likely to be complex, varying with pH, the nature of the chelating agent, and the structure of the complex.

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