Reaction of Cerium(IV) Perchlorate with Hydrogen Peroxide

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The reduction of cerium(IV) (monomer, type B) by hydrogen peroxide has been studied in 1M-$HClO_4$ and found to be rapid. A slower reaction observed previously is now believed to be most probably due to traces of cerium(IV) (polymer, type A) which reacts only slowly with hydrogen peroxide.

THE kinetics of oxidation of H_2O_2 by aquocerium(IV) ions in perchlorate ion media have been studied previously by Wells and Husain.[1] The course of the reaction was followed spectrophotometrically, using a stopped-flow apparatus, and an initial increase in the optical density followed immediately by a rapid decay was observed. These observations were attributed to the formation of an intermediate complex Ce^{IV},H_2O_2 which subsequently decays *via* an inner-sphere electron transfer path. To the generally accepted mechanism described by equations (1) and (2) the intermediate

$$Ce^{IV} + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce^{III} + H^+ + HO_2 \qquad (1)$$

$$Ce^{IV} + HO_2 \xrightarrow{k_2} Ce^{III} + O_2 + H^+ \qquad (2)$$

steps (3) and (4) were added, where it was assumed

$$Ce^{IV} + H_2O_2 \xrightarrow{k_3} Ce^{IV},H_2O_2 \qquad (3)$$

$$Ce^{IV},H_2O_2 \xrightarrow{k_4} Ce^{III} + H^+ + HO_2 \qquad (4)$$

that the latter is the rate-determining step and reaction (1) is not reversible (in contrast to previous studies [2]). The rate constant of the decay process (k_4), its dependence on acidity and concentration of reactants, and corresponding activation energy were measured. The purpose of this paper is to provide an alternative interpretation and mechanism to that proposed by Wells and Husain, and to account for the inconsistency of their observations with those of other studies.[2-4]

RESULTS AND DISCUSSION

The kinetic treatment of the cerium(IV)–hydrogen peroxide reaction by Wells and Husain was based on the assumption that, under their experimental conditions, (*a*) less than 2% of the cerium(IV) ions existed as polymeric species [4] and (*b*) the observed changes in optical density were due to reaction of H_2O_2 with monomeric [*e.g.* Ce^{4+}(aq) or $CeOH^{3+}$(aq)] rather than polymeric cerium(IV) species. The fact that at least some of the cerium(IV) ions exist as polymeric species, which yield an orange-red complex with hydrogen peroxide, was known to the authors, yet they ascribed the absorption which they found (by mistake) at 350 nm to monomeric aquocerium(IV) ions. Conclusions by Ardon and Stein,[3] regarding the existence of two types of cerium(IV) perchlorate and its properties on reaction with H_2O_2 were ignored. Cerium(IV) (type A) is formed when the hydroxide is precipitated by ammonia from cerium(IV) ammonium nitrate solution, washed free from ammonium and nitrate ions, and dissolved in 2N-$HClO_4$ on a water bath. The resulting solution thus obtained contains colloidal polymers and oxidizes H_2O_2 very slowly, yielding a transient orange-red Ce^{IV},H_2O_2 complex. Cerium(IV) (type B) is prepared on electrolytic oxidation of cerium(III) perchlorate at pH $\leqslant 0$ [*e.g.*, a solution of cerium(IV) (type A) reduced by H_2O_2]. It is composed of monomeric species which react instantaneously with H_2O_2, without generating any coloured complex.

Wells and Husain followed the reaction at a single wavelength (350 nm) where Ce^{IV}(type A),H_2O_2, Ce^{IV} (type A), cerium(IV)–hydrogen peroxide, and Ce^{IV} (type B) absorb, but not in the range 230—290 nm, where the perhydroxyl radicals also absorb. Bearing in mind that solutions of cerium(IV) perchlorate electrolytically prepared (type B) are metastable,[3,5] even at relatively low pH values, and tend to convert into cerium(IV) (type A) *via* an irreversible process, we believe that the authors misinterpreted their results in relating them to monomeric cerium(IV) ions. The appearance and decay of the transient absorption at 350 nm was probably due to the reaction of colloidal polymer [3-5] formed in various amounts in their solutions.

In order to check this assumption, we repeated the experiments of Wells and Husain and studied the reactions of individual 5×10^{-4}M-cerium(IV) solutions of type A, type B, and type B 'contaminated' with 8% type A, with an excess of H_2O_2 (5×10^{-3}M) in a stopped-flow system. [Type B and A solutions were prepared from cerium(III) perchlorate (G. F. Smith Chemical Co.) according to Smith *et al.*[6] and Ardon.[3]] The reactions were carried out in 1M-$HClO_4$ at 25 °C, and changes in optical density were studied over the whole range of wavelengths from 215 to 400 nm (experimental details of the system are described elsewhere [2]).

From the optical density changes at 250, 280, and 350 nm (Figure) we draw the following conclusions. In the case of cerium(IV) (type B), no cerium(IV) ions

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[1] C. F. Wells and M. Husain, *J. Chem. Soc.* (*A*), 1970, 1913.

[2] G. Czapski and A. Samuni, *Israel J. Chem.*, 1969, **7**, 361; G. Czapski, H. Levanon, and A. Samuni, *ibid.*, p. 375; A. Samuni and G. Czapski, *ibid.*, 1970, **8**, 551.

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[4] T. J. Hardwick and E. Robertson, *Canad. J. Chem.*, 1951, **29**, 818, 828.

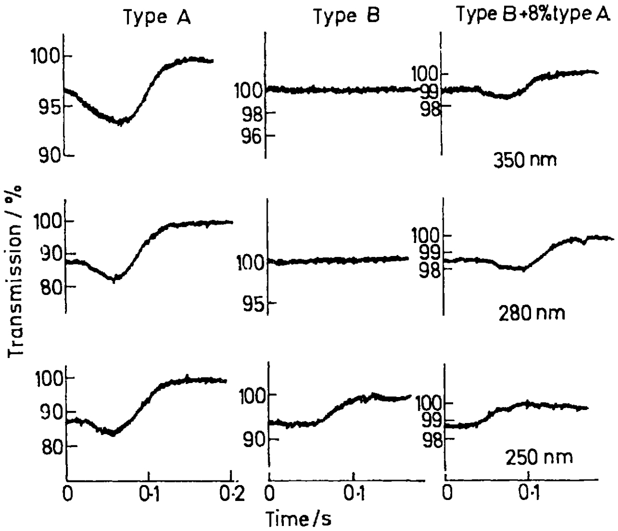
[5] M. Ardon, Ph.D. Thesis, The Hebrew University, Jerusalem, 1957.

[6] C. F. Smith, G. Frank, and A. E. Kott, *Indian Eng. Chem.* (*Analyt.*), 1940, **12**, 268.

were left on the arrival of the flowing reaction mixture at the observation point [indicating that reaction (1) is too fast to be measured]. The only species surviving at the observation point are the HO_2 radicals, which in turn decay *via* the self-recombination reaction (5) [2,7] (HO_2 absorbs at 250 nm while at $\lambda > 280$ nm only the Ce^{IV} in its various forms absorbs). On the other hand, with cerium(IV) (type A) formation and some decay of transient absorption were observed at $250 < \lambda < 350$ nm, as has been previously reported.[1,3] The results and absorption spectrum of the Ce^{IV}(type A),-H_2O_2 complex are consistent with those of Ardon,[3] indicating that Wells and Husain actually followed the reaction of polymeric cerium(IV) perchlorate with H_2O_2 rather than that of the monomeric ions.

$$HO_2 + HO_2 \xrightarrow{k_5} H_2O_2 + O_2 \qquad (5)$$

Ca. 8% of type A was then added to cerium(IV) (type B) solution and the above experiments repeated (Figure). On replacing spectrophotometric detection by that of e.s.r. spectrometry, a similar behaviour was obtained: the usual spectrum of HO_2 [2,7] could be detected only when H_2O_2 was oxidized by cerium(IV) (type B), a new asymmetric e.s.r. signal appearing when type A was used. The results shown in the Figure confirm our hypothesis that the appearance of the transient absorbance occurs on using cerium(IV) perchlorate solutions which are not free of colloidal polymeric species; this invalidates the kinetic treatment of Wells and Husain.[1] [The experiments made with cerium(IV) (type A), as shown previously,[5] are not reproducible due to the undefined chemical nature of the colloidal species involved.] The disagreement between the results of Ardon [3] and Wells [1] regarding the rate of decay of the Ce^{IV},H_2O_2 transient complex is therefore explained.



Oscilloscope traces of optical density changes at 250, 280, and 350 nm for the reaction of 10mM-H_2O_2 with 1mM-Ce^{IV} (type A, type B, or a mixture of 8% type A with 92% type B)

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