

## THE PHOTOLYSIS OF CONCENTRATED PERCHLORIC ACID SOLUTIONS

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### Summary

The production of  $\text{ClO}_2$  after the photolysis of 6 M perchloric acid ( $\text{HClO}_4$ ) has been identified on the basis of its absorption spectrum. Using 3 M  $\text{HClO}_4$ , no absorption corresponding to  $\text{ClO}_2$  was observed, but rather a weaker absorption at around 300 nm attributed to  $\text{ClO}^-$  was identified.

In order to study the possible photo-oxidation of manganese(II) in aqueous solution under conditions where the anticipated product, manganese(III), is stable, we have used 6 M perchloric acid ( $\text{HClO}_4$ ) as the solvent. After a 0.2 M solution of  $\text{Mn}(\text{ClO}_4)_2$  in 6 M  $\text{HClO}_4$  in a 1 cm quartz cuvette had been irradiated with a low pressure mercury lamp for about 30 min, an absorption centered at about 470 nm, characteristic of manganese(III), was observed. Another absorption, centered at about 358 nm, where manganese(III) does not absorb, was also observed. With time, this second absorption increased until it dominated the spectrum. Irradiation of the solution through an interference filter (23 nm bandpass) centered at 260 nm produced no absorbing species using either the 1 cm cell or a 10 cm cylindrical cell, suggesting that the strong mercury line at 254 nm was not responsible for the photolysis.

In order to clarify what was happening, we have carried out a brief study of the photolysis of  $\text{HClO}_4$  using a low pressure mercury lamp. The results of one run using 6 M  $\text{HClO}_4$  are shown in Fig. 1. The 1 cm absorption cell was irradiated at a distance of about 1 cm from its center for 10 min on each of the two transparent sides. It was then placed in a spectrophotometer and a spectrum was taken immediately and, without further irradiation, after 30, 90 and 120 min. In a similar run the maximum absorption at 358 nm was 0.05 initially, 0.13 after 10 min, 0.22 after 20 min and finally reached a maximum of 0.74 after several hours. The absorption then slowly decreased, and no additional spectral features were observed on its decay.

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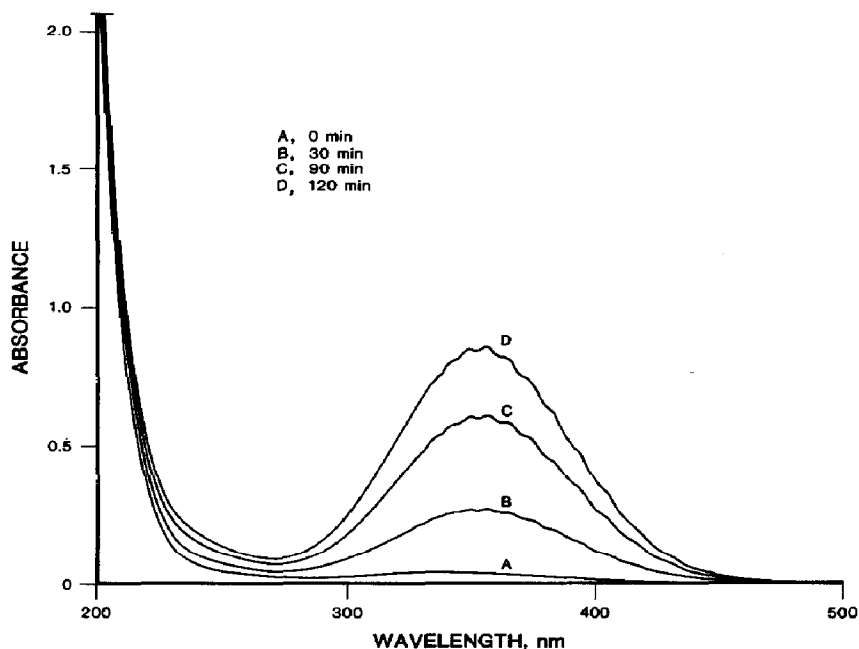
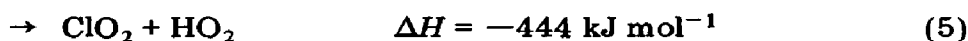
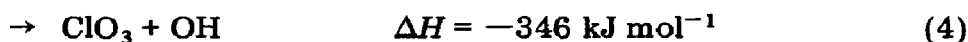
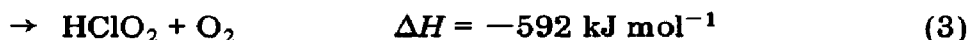
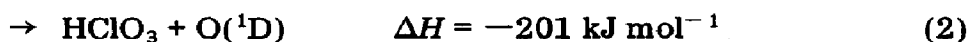


Fig. 1. Absorption spectrum of 6 M  $\text{HClO}_4$  after 20 min photolysis. The spectra were taken at the indicated times after the termination of photolysis.

This absorption spectrum appears to be identical with that reported for  $\text{ClO}_2$  [1, 2], which has a molar absorptivity at 358 nm of about  $1250 \text{ M}^{-1} \text{ cm}^{-1}$  [3], so that the maximum amount produced from the 20 min photolysis of 6 M  $\text{HClO}_4$  was about  $6 \times 10^{-4} \text{ M}$ . The production of  $\text{Cl}^-$  by the photolysis was suggested by the production of a white precipitate on the addition of silver nitrate.

A similar experiment to that described above was also carried out using 3 M  $\text{HClO}_4$ . No significant absorption at 358 nm was observed. The sensitivity of the spectrophotometer would have easily allowed the measurement of a relative absorption of 0.01. Therefore, the maximum amount of  $\text{ClO}_2$  produced from the photolysis of 3 M  $\text{HClO}_4$  was 100 times less than that measured for 6 M  $\text{HClO}_4$ . An absorption centered at about 300 nm was observed, however, which slowly increased to about 0.02 and then faded after a few hours. This is possibly due to the hypochlorous ion,  $\text{ClO}^-$  [2].

$\text{HClO}_4$  does not have a strong absorption at 254 nm. Irradiation with 254 nm radiation does not lead to the  $\text{ClO}_2$  spectrum in the presence of manganese(II). Therefore, the photolysis of  $\text{HClO}_4$  most probably arises because of the absorption of the 185 nm line from the low pressure mercury lamp. At that wavelength, any of the following reactions are possible [4] (the values for  $\text{ClO}$ ,  $\text{O}(^3\text{P})$ ,  $\text{O}(^1\text{D})$ ,  $\text{OH}$  and  $\text{HO}_2$  are for the gas phase) (if protonation equilibria are neglected):

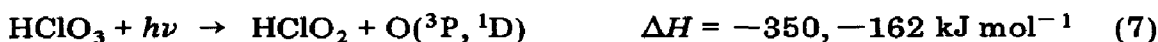


From a study of the photolysis of the perbromate ion [5] it was concluded that the results could be explained using the simple primary reaction



with secondary reactions yielding  $\text{BrO}_2$ ,  $\text{BrO}_2^-$ ,  $\text{HO}_2^-$  and  $\text{O}_2$ .

In our system the chlorate ion or  $\text{HClO}_3$  could undergo further photolysis,



and these products in turn could be photolyzed:



The radiation chemistry of the perchlorate ion has been studied by several workers [6 - 10]. In general, the results appear to indicate that chlorate ions are the major product. In a recent pulse radiolysis experiment [7] a transient absorption with a maximum at 410 nm was assigned to  $\text{ClO}_3$ . A shoulder at 280 nm was ascribed to  $\text{ClO}$ .

Behavior similar to that described here was observed in a radiolysis experiment using 60 keV X-rays [6]. When the concentration of  $\text{HClO}_4$  was greater than 6 M,  $\text{ClO}_2$  was formed, with its concentration increasing slowly after irradiation had been terminated. This is similar to our observation that  $\text{ClO}_2$  is formed at 6 M  $\text{HClO}_4$  but not at 3 M  $\text{HClO}_4$ . In the only previous work on the photolysis of perchloric acid, all that was reported was that oxygen was evolved [11].

It is apparent from Fig. 1 that, if  $\text{ClO}_2$  is produced directly in the photolysis of  $\text{HClO}_4$  to a significant extent, it is in turn photolyzed. The  $\text{ClO}_2$  which is observed obviously arises from slow secondary reactions. Even if the primary photolytic step is only reaction (2), the various secondary reactions and photolysis will lead to a complex mixture. This, together with the limited amount of data available, prevents certain identification of the precursor to  $\text{ClO}_2$ . A plausible source, however, is  $\text{HClO}_2$  which is known to undergo slowly self-reaction to yield  $\text{ClO}_2$  [3]. The rate of this reaction is observed to increase with decreasing pH, although not to such a dramatic extent as to explain easily the difference between the photolysis of 6 M and 3 M  $\text{HClO}_4$ .

observed here. The mechanisms which have been proposed for the self-reaction of  $\text{HClO}_2$ , however, include many of the other possible products of perchloric acid photolysis. Therefore, in order to understand these results, considerably more data are needed, particularly the identification of at least the more stable intermediates and a careful study of the dramatic effect of acid concentration.

## References

- 1 F. Stitt, S. Friedlander, H. J. Lewis and F. E. Young, *Anal. Chem.*, **26** (1954) 1478.
- 2 T. Chen, *Anal. Chem.*, **39** (1967) 804.
- 3 G. Gordon, R. G. Kieffer and D. H. Rosenblatt, *Prog. Inorg. Chem.*, **15** (1972) 201.
- 4 D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm, *NBS Tech. Note 270-3*, 1968 (National Bureau of Standards, U.S. Department of Commerce).
- 5 U. K. Klänig, K. J. Olsen and E. H. Appelman, *J. Chem. Soc., Faraday Trans. I*, **71** (1975) 473.
- 6 L. T. Bugaenko and Y. V. Maksimov, *Zh. Fiz. Khim.*, **40** (1966) 1813.
- 7 C. Ferradini, J. Pucheault and R. Julien, *J. Chim. Phys.*, **72** (1975) 121.
- 8 D. Katakis and J. Konstantatos, *J. Phys. Chem.*, **72** (1968) 2054.
- 9 D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68** (1964) 3107.
- 10 J. Konstantatos and D. Katakis, *J. Phys. Chem.*, **71** (1967) 979.
- 11 J. Barrett, *Ph.D. Thesis*, University of Manchester, 1959, quoted in M. J. Blandamer and M. F. Fox, *Chem. Rev.*, **70** (1970) 591.