The Oxidation of Fe^{2+} by Ultrasound

By Satya PRAKASH, Jata Dhari PANDEY and Rajendra SINGH

(Received January 10, 1964)

Among the various unusual chemical effects produced by high frequency intense sound waves, much interest has been shown recently in the oxidation reactions of aqueous solutions of inorganic salts, e.g., the oxidation of iodide ions,[1-8] the oxidation of ferrous ions,[9-14] the oxidation of cerous ions,[13,14] and the reduction of acidified potassium permanganate[15] and neutral ferrocyanide.[14,15]

The present paper will report on a study of the oxidation of acidic ferrous ammonium sulphate by the intense ultrasonics of 1 Mc.

Experimental

In the present investigation, the source of ultrasonic power was a commercially-available ultrasonic generator, Mullard Type E-7562, which is meant for all purposes requiring high power ultrasonic waves at high frequencies. In addition to the generator, the other accessories were a suitable ultrasonic bath, a proper reaction vessel, and an easy procedure for the coupling of the reaction vessel with the transducer. The basic circuit of the oscillator is shown in Fig. 1. It consists of mainly a number of condensers (C), a tuning coil (L) which is of a variable type and which can be detached from the instrument and replaced by another coil designed for another frequency, and Mullard's silica envelop, triode-type TYS_4-500, which is used to generate radiofrequency power. The oscillator was self-biased, and meters were provided to read the cathode current up to 1 amp., high tension up to 3.500 V., and radiofrequency output voltage up to 10 kV. The transducer used was made of barium titanate ceramics with a frequency of 1 Mc. The major portion of the work was done at a fixed electrical output to the transducer, except when the effect of sonic intensity was to be studied. The reaction vessel was a 250-ml. flat bottomed jena glass battle with ground glass stopper. This reaction bottle was held vertically above the transducer in a water bath and the position so adjusted as to produce a maximum fountain inside the vessel when the ultrasound passed through. The other details of the experimental technique have already been described in previous communications.[16,17] The temperature was kept at 31.5 ± 0.1°C.

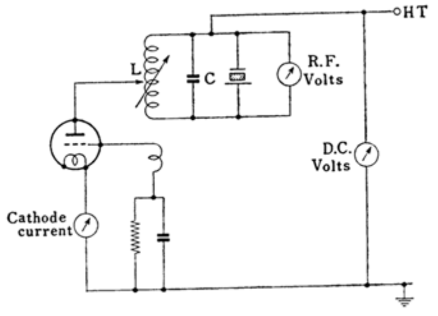

Fig. 1. Simplified oscillator circuit of ultrasonic generator.

Materials. — A stock solution of 0.1 N ferrous ammonium sulphate (A. R., B. D. H.), acidified with A. R. sulphuric acid, was prepared in doubly-distilled water. A ceric sulphate solution of about 0.1 N was prepared from B. D. H.-quality salt by dissolving 34 g. of the salt in 50 ml. of 1 : 1 sulphuric acid (A. R. quality) and making it up to 500 ml. with doubly-distilled water. This solution was then standardised by titrating it against a standard ferrous ammonium sulphate solution, using N phenylanthranilic acid in alcohol as an indicator.

Results and Discussion

In a series of experiments, 25 ml. portions of ferrous ammonium sulphate solutions of known concentrations were placed in the reaction bottle and subjected to ultrasonic waves for different periods of time. The radiofrequency output voltage was kept constant, equal to 2.0 kV. (approx.). As a result of the ultrasonic exposure, the ferrous content of the solution changed to ferric; this was estimated

---

[1] H. Liu and S. Wu, *J. Am. Chem. Soc.*, **56**, 1005 (1934).

[2] W. T. Richards and A. L. Loomis, ibid., **49**, 3086 (1927).

[3] J. Bhar, *J. Sci. Ind. Res.* (*India*), **1**, 106 (1943).

[4] N. Sata and K. Nakashima, This Bulletin, **18**, 220 (1943).

[5] A Weissler and H. W. Cooper, *Mfg. Chemist.*, **19**, 505 (1948).

[6] R. O. Prudhomme and P. Grabar *J. chim. phys.*, **43**, 323 (1949).

[7] A. Weissler, H. W. Cooper and S. Snyder, *J. Am. Chem. Soc.*, **72**, 1769 (1950).

[8] A. Weissler, *J. Acoust. Soc. Am.*, **25**, 651 (1953).

[9] N. Miller, *Trans. Faraday Soc.*, **46**, 546 (1950).

[10] N. Miller, *J. chim. phys.*, **48**, 242 (1951).

[11] I. E. El'Piner and A. V. Sokol'skaya, *Dok. Akad. Nauk. S. S. S. R.*, **129**, 202 (1960).

[12] M. Haissinsky and R. Julien, *J. chim. phys.*, **57**, 664 (1960).

[13] A. Weissler, *J. Acoust. Soc. Am.*, **32**, 283 (1960).

[14] M. Haissinsky and R. Rivayrand, *J. chim. phys.*, **59**, 623 (1962).

[15] S. Witekowa, *Roczniki Chem.*, **36**, 693 (1962).

[16] S. Prakash and S. C. Srivastava, *J. Ind. Chem. Soc.*, **35**, 797 (1958).

[17] S. Prakash and S. Prakash, *Z. phys. Chem.*, **221**, 145 (1962).

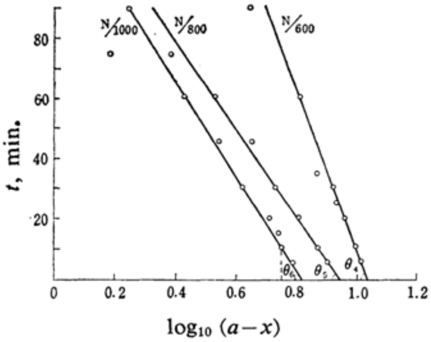

Fig. 2. Plot of $\log_{10}(a-x)$ vs. t.

a is the initial concentration of ferrous ammonium sulphate and x, the change in concentration after t min.

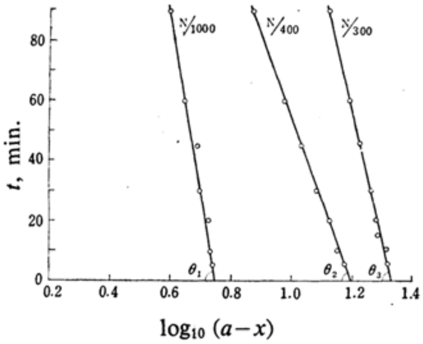

Fig. 3. Plot of $\log_{10}(a-x)$ vs. t.

TABLE I. KINETICS OF OXIDATION OF Fe^{2+} BY ULTRASOUND AT DIFFERENT CONCENTRATIONS OF $FeSO_4(NH_4)_2SO_4\cdot 6HO_2$

Initial concn. of $FeSO_4(NH_4)_2SO_4\cdot 6H_2O$	$k_1\times 10^3$ min^{-1}	
	$k_1=(2.303/t)\cdot \log_{10}(a/(a-x))$*	Graphically from slopes (Figs. 2 and 3)
N/100	3.779	4.145
N/300	5.411	5.200
N/400	8.407	8.171
N/600	8.925	8.348
N/800	16.885	15.545
N/1000	18.520	19.969

* a Initial concentration
x Concentration at time t

volumetrically from time to time. The results are shown in Figs. 2 and 3. A study of the kinetics showed that the reaction is of the first order. The rate constant obtained is shown in Table I.

A perusal of the table will show that the order of the reaction does not change with the concentration and that the rate increases considerably at higher dilutions of ferrous ammonium sulphate. The values of k_1 as calculated from the equation and from the graph (Figs. 2 and 3) are approximately the same, with a maximum error of about 7 per cent. It can also be predicted that, when the concentration is decreased ten times, the values of k_1 increase by about five times, when the concentration of the solution is halved, k_1 is almost doubled, and so on.

We also investigated the effect of the intensity of ultrasound on the rate of reaction. The results are shown in Fig. 4, where the variation in the constants with acoustic power is given. At a fixed concentration (N/500) of ferrous ammonium sulphate, the kinetics of the reaction was studied by varying the R. F. output. The order velocity constants, as calculated both theoretically and graphically, are given in Table II.

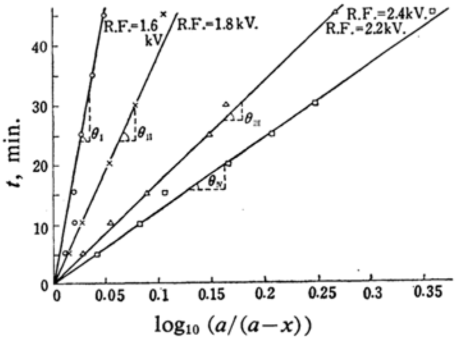

Fig. 4. The effect of ultrasonic intensity.

TABLE II. KINETICS OF REACTION AT DIFFERENT INTENSITIES OF ULTRASOUND

R. F. output kV.	$k_1\times 10^3$ min^{-1}	
	$k_1=(2.303/t)\cdot \log_{10}(a/(a-x))$	From graph (Fig. 4)
1.6	3.048	2.530
1.8	6.266	6.073
2.2	13.685	13.160
2.4	18.684	18.679

It is clear from the above data, as well as from Fig. 4, that the sonic intensity has a pronounced effect on the rate of reaction. The values of k_1 continuously increase with an increase in the R. F. output voltage. Further, it may also be concluded that the increase in k_1 values is slower at lower powers than at higher ones.

It is well known that chemical reactions do not occur at very low intensities. Nearly all the observed chemical effects of ultrasonic irradiation in liquid systems occur only at intensities sufficient to induce cavitation within the system. Cavitation is only initiated when and where the pressure amplitude is greater than the cavitation threshold amplitude. Above this threshold value the reaction rate increases continuously. The increase in intensity will result in an increase in the cavitational intensity, which may be defined as the capability of cavities to bring about chemical reactions. It is evident that, as the number of cavitational holes increases, more and more cavities will form and collapse, resulting in an increase in the rate of the reaction. In the experimental procedure, it was found in most cases that the initial rate (k_1) was slightly higher than the rates during the progress of the reaction. The higher initial rate is most probably connected with the absence of scattering gas bubbles in the very beginning of the reaction.

The formation of hydrogen peroxide from water, when it is exposed to ultrasonic waves, is a complex process, involving many interrelated reactions. The most probable mechanism of the sonolysis of water is the free radical mechanism proposed recently by Weissler,[18)] Lindström et al.,[19)] Prudhomme et al.[20)], and others.[14,21)] They have all suggested the formation of H_2O_2 and some freee radicals, such as H, OH and HO_2. According to Weissler, the various steps involved may be written as:

$$H{\cdot}OH \rightarrow H + OH$$

$$H + H \rightarrow H_2$$

$$OH + OH \rightarrow H_2O_2$$

$$H + H_2O_2 \rightarrow H_2O + OH$$

$$OH + H_2 \rightarrow H_2O + H$$

In oxygenated solutions, additional hydrogen peroxide may be formed by a route involving, perhydroxyl (HO_2) radical:

$$H + O_2 \rightarrow HO_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

When a solution of ferrous ammonium sulphate in water is exposed to ultrasonic waves, the formation of H, OH, HO_2 and H_2O_2, as has been described above, is the primary step. Since the cavitation bubbles collapse and those formed at the solid nuclei are weak, the direct decomposition of ferrous ammonium sulphate is doubtful. The presence of a gas[21-25)] is always a necessary condition for the occurrence of cavitational chemical reactions. Most probably, the primary decompositions due to the cavitation take place in the gas phase inside the cavitation bubbles.[26,27)] Therefore, the oxidation of potassium iodide or of ferrous ammonium sulphfate may be regarded as a secondary reaction brought about by the products of the primary reactions.

The major pioneering work introducing the concept of inorganic free radicals in the field of reaction kinetics was that of Haber and Weiss.[28-29)] We have made use as follows of the steps suggested to explain the oxidation mechanism:

Heat, kcal.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$

$$\rightarrow Fe^{3+}{\cdot}OH^- + OH \qquad -(5\text{ to }7)$$

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \qquad +42$$

$$Fe^{2+} + HO_2 \rightleftarrows Fe^{3+} + HO_2^- \qquad +29$$

The $Fe^{3+}{\cdot}OH^-$ radical may further combine as:

$$Fe^{3+}{\cdot}OH^- + OH \rightarrow Fe^{2+} + H_2O_2 \qquad +(5\text{ to }7)$$

The heats of reaction are taken from Uri's review.[30)]

The auto-oxidation of Fe^{2+} may also take place due to activated oxygen:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^-$$

At a lower concentration the formation of chain carriers (H_2O_2, HO_2 and OH) is enhanced, resulting in an increase in the reaction rate.

Summary

With the help of Mullard's high frequency ultrasonic generator, type E-7562, with a barium titanate transducer with a frequency of 1 Mc, the oxidation of an acidic ferrous ammonium sulphate solution has been studied. The kinetics of the reaction, at six different concentrations of a ferrous ammonium sulphate solution and at four different ultrasonic intensities has been investigated. The reaction has been found to obey the first order kinetics. A probable mechanism based on the Haber-Weiss work has also been proposed.

The authors wish to express their deep sense of gratitude to the Council of Scientific and Industrial Research, India, for supporting

---

18) A. Weissler, *J. Am. Chem. Soc.*, **81**, 1077 (1959).

19) O. Lindström and O. Lamm, *J. Phys. & Colloid Chem.*, **55**, 1139 (1951).

20) R. O. Prudhomme and P. Grabar, *J. chim. phys.*, **46**, 323 (1949).

21) B. H. Jennings and S. N. Townsend, *J. Phys. Chem.*, **65**, 1574 (1961).

22) K. Littlewood, *J. Roy. Inst. Chem.*, **86**, 78 (1962).

23) S. C. Srivastava and N. Berkowitz, *Can. J. Chem.*, **41**, 1787 (1963).

24) V. Griffing, *J. Chem. Phys.*, **18**, 997 (1950).

25) A. Weissler, ibid., **18**, 1513 (1950).

26) S. C. Srivastava and N. Berkoweitz, *Can. J. Chem.*, in press.

27) O. Lindström, *J. Acoust. Soc. Am.*, **27**, 654 (1955).

28) F. Haber and J. Weiss, *Naturwiss.*, **20**, 948 (1932).

29) F. Haber and J. Weiss, *Proc. Roy. Soc.*, **A147**, 332 (1934).

30) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

their work, and for the award of a Senior Research Fellowship to one of them (Dr. Jata Dhari Pandey).

Department of Chemistry
University of Allahabad
Allahabad, India