

### Chemical Reactions initiated by Ultrasonic Waves

I HAVE been engaged in the study of a number of reactions in solution caused by ultrasonic waves.

*Sono-chemical decomposition of organic halides.* Under the influence of ultrasonic waves aqueous solutions of chloroform, carbon tetrachloride, dichloro- and diiodo-methane, dichloro- and dibromoethane, and ethyl chloride, bromide and iodide have been found to liberate halogens<sup>1</sup> in both the ionic and the molecular states (tested by silver nitrate solution, potassium iodide and starch indicator). Five of these have been studied in detail and the results are summarized here (compare refs. 2-7).

(1) Aqueous solutions of dichloromethane, chloroform, carbon tetrachloride, dichloroethane and ethyl bromide subjected to ultrasonic waves (1-2 Mc./s., 225 watts electrical input to the transducer) liberate halogens, simultaneously producing polymerized solids. None of them, except chloroform, decomposes in the pure state.

(2) In all five cases only a part of the total halogen is liberated and does not seem to increase much with long exposures. The liberation of halogens increases with dilution.

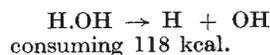
(3) A considerable bulk effect is observed, probably due to the direct load of the liquid on the transducer.

(4) Organic liquids such as alcohol and acetone retard the reaction, and beyond a certain concentration the reactions stop altogether.

(5) Ultrasonic intensity influences the reaction; at higher power output the reactions are accelerated.

(6) The decompositions are of zero order and in four cases (CH<sub>2</sub>Cl<sub>2</sub> not tried) the reactions proceed faster at lower temperatures.

(7) The primary sono-chemical reactions postulated are:



and



consuming 68 kcal. for C—Cl  
and 54.5 kcal. for C—Br

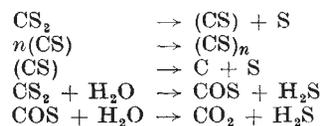
where X is a halogen atom.

These reactions are supposed to be followed by hydrolysis and polymerization.

*Sono-chemical decomposition of organic sulphides.* The bond-strength between carbon and sulphur is 54.5 kcal., which is approximately equal to that between carbon and bromine in organic aliphatic halides. It was believed, therefore, that organic sulphur compounds would decompose in the same way as organic halides, liberating sulphur. The simplest organic sulphide, namely, carbon disulphide, was exposed to ultrasonic waves in the pure state as well as in aqueous solutions. In the pure state there was no detectable liberation of sulphur, whereas in aqueous solution a brown-coloured colloidal sol which was very stable was obtained. Similarly, with aqueous solutions of ethyl disulphide a white-coloured colloidal sol, which was very stable, was obtained. It was analysed qualitatively and the colloidal sulphur particles were observed to be of a different size-range from those from carbon disulphide. The brown sol treated with ammonia gave a brown colour, and with sulphuric acid a pink colour. When the solid obtained by centrifuging was treated

with various organic solvents, a black residue was obtained which was suspected to be carbon.

On this basis the following mechanism for the decomposition of carbon disulphide is suggested:



*Inorganic reactions initiated by ultrasonic waves.* I exposed redistilled water to ultrasonic waves and observed a change in conductivity (after 1½ hr. exposure, from  $4 \times 10^{-6}$  to  $1.15 \times 10^{-4}$  ohm<sup>-1</sup>cm.<sup>-1</sup>), but no conclusive reactions due to the presence of hydrogen peroxide in the free state were obtained. A very dilute acidic solution of potassium permanganate was decolorized, but a very dilute acidic solution of potassium dichromate covered with a layer of ether showed no change in colour. When a slightly higher concentration of potassium permanganate was used it gave a sol at shorter periods of exposure, and after long exposure gave a brown precipitate, probably an oxide of manganese. A titanous solution exposed to ultrasonic waves was oxidized to the titanous state, losing its violet colour, but a cerous solution did not turn orange, indicating that it had not been oxidized to the ceric form. A ferrous solution was converted to the ferric state, identified by the usual potassium thiocyanate and potassium ferricyanide tests.

The experimental work reported here was carried out in the Chemical Laboratories of the University of Allahabad.

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### Chemistry and Clay Mineralogy of a Soil Sample from Antarctica

A SAMPLE of soil, scraped up by Mr. A. S. Helm from Scott Base, McMurdo Sound, has been analysed by this laboratory. The material contained many well-rounded blue-grey stones of basaltic and arenaceous origin, the majority being basaltic. It was apparently derived from the basaltic rocks which outcrop in the area and mixed with material from sedimentary sources in the vicinity. No humus was apparent to the eye but the sample contained a small piece of moss as well as some bacteria (J. D. Stout, personal communication) and is thus justifiably regarded as a soil. Of the material collected, 98.6 per cent was less than 25 mm. in diameter and 64 per cent less than 2 mm. Only 2.6 per cent was less than 0.066 mm. and less than 1 per cent of clay was present.

The high pH value (1:2.5 water suspension) is apparently caused by the presence of calcium car-