

co-operation in allowing us to use the Laboratory's electromagnet.

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CHEMISTRY

Effect of Ultrasonic Insonation on the Carbon Tetrachloride-Water-Dissolved Helium System

It was the purpose of this study to obtain more evidence regarding the effect of ultrasonics on chemical reactions, and to determine the relationship between the reaction yield and solubility of dissolved gas in the system. Griffing¹ found that gases of different solubilities have different thresholds of cavitation; but no attempt was made to ascertain the effect of varying the solubility of a particular gas.

The system studied was the carbon tetrachloride-water-dissolved helium system. In order to ensure that the helium was the gas responsible for any reaction that might be observed, the water used was purified and degassed. Carbon tetrachloride was added and the mixture was vigorously agitated. Helium was then bubbled through, and after settling the substrate consisted of two distinct phases. The phase rich in carbon tetrachloride was used for the experiments. The carbon tetrachloride-water-dissolved helium mixture was then transferred (in a helium atmosphere) to a specially designed reaction vessel, one side of which was covered with a polyester film of high sound permeability. This served as a sound window.

The reaction mixture was exposed to 1,000 kc./s. sound energy at a power output of 7.20 watts/sq. cm. The sound was transmitted through a plain tap water medium from crystal to vessel. This water was circulated and served also as a constant-temperature bath. The distance between the crystal and reaction vessel surface was maintained the same for each run. This assured uniform sound absorbance by the sample. The samples after insonation were analysed for chlorine by addition of potassium iodide solution and the titration of the liberated iodine with sodium thiosulphate solution. Starch was used as indicator. It was found that the pH change brought about by the reaction was sufficient to supply the acid medium need for the above analysis.

Samples which were insonated immediately after they were transferred from the preparation apparatus to the reaction vessel gave erratic results. Samples which were transferred and allowed to stand 12 hr. before insonation gave much greater reproducibility. Griffing¹ observed a similar phenomenon. Different final concentrations of chlorine, due to insonation, were observed for vessels which were

completely filled and those which were partially filled with reaction mixture (the vapour space being filled with helium). In addition to chlorine, it was thought that trace amounts of hexachloroethane could be detected.

The formation of chlorine and hexachloroethane from the reaction mixture, in the absence of oxygen, indicates a free-radical mechanism. This could well be due to the break-up of the water molecule as a result of local heating due to the adiabatic compression of the dissolved gas, as Griffing has suggested².

The different yields observed for partially filled and completely filled vessels can be ascribed to the variation in gas solubility with pressure. Ultrasonic insonation is a degassing process. It is obvious that the residual pressure in a vessel which was originally filled is much greater than the pressure in a vessel which was partially filled. According to Griffing's theory with regard to the effect of solubility on cavitation³, the yield of chlorine would be greater at low pressures and lower at high pressures. The data show that the yield for filled vessels was lower than that for partially filled vessels. This supports the solubility theory of Griffing, using only a single gas. This eliminates any doubt which might have arisen due to the varying of solubility with different gases and thereby changing other physical properties as well.

The cause of the erratic results after sample transfer was probably nucleation—the formation of centres of gas bubble agglomeration. This would occur in random fashion for each run, thereby introducing a lack of similarity in sample preparation.

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¹ Griffing, Sette, Sullivan and Majowicz, "Experiments on Cavitation and Related Reactions" (Catholic University, Washington, D.C.) (unpublished).

² Griffing and Fitzgerald, *J. Chem. Phys.*, **25**, 5 (1956).

Optical Rotatory Dispersion Studies on Partially Methylated Cellulose

ROTATORY dispersion studies have been conducted on a large number of proteins and polypeptides¹⁻³. We wish to report some preliminary studies on the rotatory dispersion of polysaccharides. The material used for this work was 'Methocel' (registered trade mark of the Dow Chemical Company, Midland, Michigan) supplied by the Dow Chemical Co. 'Methocel' is a partially methylated cellulose which has the characteristic of being more soluble in cold water than in hot water. This investigation was carried out on material with an intrinsic viscosity of 1.6 (corresponding roughly to a molecular weight of 35,000) and a methoxyl analysis of 29.5 per cent (1.8 OCH₃ groups/anhydroglucose unit). The method of solubilizing this particular polysaccharide consisted in dispersing the material in boiling water and allowing it to cool to room tem-