

$k = 5.120 \times 10^5$ dyn cm⁻¹ have been computed, yielding the u value listed in Table 1.

The C—C distances. An approximate calculation of the mean amplitude of vibration of the C—C distances have been worked out by adopting the equilateral triangle model (CH₂)₃ for cyclopropane. The following explicit formula has been derived

$$u_{C-C}^2 = (h\mu_X^{1/2} / 4\pi 3^{1/2}) [(k + 2k')^{-1/2} + 2^{1/2} (k - k')^{-1/2}]$$

k denotes here the principal C—C stretching force constant and k' the interaction force constant between two C—C stretches. μ_X is the inverse mass of CH₂. In this case it did not affect the result appreciably when the interaction constant was made equal to zero. Consequently, the formula could be simplified to

$$u_{C-C}^2 = h\mu_X^{1/2} (1 + 2^{1/2}) / 4\pi(3k)^{1/2}$$

From the fundamentals⁵ (A₁) 1189 and (E') 868 cm⁻¹, the value $k = 4.064 \times 10^5$ dyn cm⁻¹ have been obtained, and the resulting u value is listed in Table 1.

It is planned to perform more rigorous calculations of u -values in cyclopropane, including also the other C—H distances as well as the H—H distances.

1. Almenningen, A., Bastiansen, O. and Fernholt, L. *Unpublished*.
2. Bartell, L. J. *Chem. Phys.* **23** (1955) 1219.
3. Almenningen, A. and Bastiansen, O. *Research Correspondence* **9** (Sept. 1958).
4. Cyvin, S. J. *Acta Chem. Scand.* **12** (1958). *In press*.
5. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, N.Y. 1945.

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A Photoactivated Polymerization of Hexabromoethane

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Investigations of the photoactivated exchange reaction of bromine between hexabromoethane and free bromine in carbon tetrachloride solution by means of the

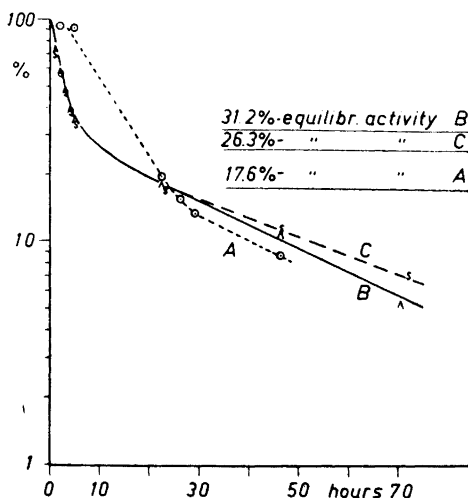


Fig. 1. Activity in organic phase as percentage of activity at zero time.

- Curve A: [C₂Br₆*] = 1.04 mmole/l, [Br₂] = 14.56 mmole/l. In air, 50°C.
 Curve B: [C₂Br₆*] = 1.39 mmole/l, [Br₂] = 9.18 mmole/l. In carbon dioxide atm, 20°C.
 Curve C: [C₂Br₆*] = 1.39 mmole/l, [Br₂] = 11.50 mmole/l. In nitrogen atm, 20°C.

radioactive isotope ⁸²Br, indicated a polymerization reaction occurring coincident with the exchange reaction.

A condensation of carbon tetrabromide to hexabromoethane has been described earlier¹, but this work did not indicate any polymerization of the hexabromoethane.

Procedure: Free bromine and hexabromoethane were irradiated in the pile, dissolved in carbon tetrachloride solutions and irradiated by an electric bulb. The solutions were in turn kept in a closed glass flask filled with dry, purified nitrogen or carbon dioxide.

The apparatus was placed in a thermostatic bath, and filling and removing of aliquots could take place without letting air into the system. Aliquots were taken at different times and free bromine extracted with reducing, aqueous solutions of sodium bisulphite. The organic phases containing the hexabromoethane were washed with distilled water, and the radioactivity measured with a scintillation counter.

The hexabromoethane was prepared according to the method of Mouneyrat² and recryst-

tallized repeatedly from carbon disulphide solutions. The carbon tetrachloride was purified by irradiation in the presence of chlorine and chlorine dioxide, followed by fractional distillations².

Results: In several experimental series the radioactivity in the hexabromoethane was found to fall far below the calculated exchange equilibrium values. Fig. 1 shows some typical results corrected for radioactive decay. Corresponding series in darkness at 20°C and 50°C showed no exchange in organic bound activity after 50 h.

Solutions containing radioactive hexabromoethane with no free bromine added, were irradiated 45 h and 48 h, respectively, with no change in organic bound activity. One of the solutions was then treated with dry chlorine gas and again exposed to light. This caused a continuous fall in organic bound activity followed for 143.5 h. The activity had fallen to 4.8 % of the original activity.

The other solution was kept in light over night. The reaction had then started, and the solution was coloured by free bromine. Similar results were obtained in other runs. Some free bromine, however, up to 20–30 % of the total activity, depending on the pile flux, is always present in the hexabromoethane due to recoil reactions. In all series the reaction was followed by a marked increase in pressure owing to liberated bromine.

Different samples of the reaction products were isolated. One sample was prepared from a nearly saturated solution of hexabromoethane in 70 ml of carbon tetrachloride. 3 ml of bromine were added. The solution was irradiated in nitrogen atmosphere for one week, and the reaction was followed by a manometer. A white, flaky material was then floating on the surface. The solution was carefully evaporated to dryness, and the residue washed with alcohol. Another sample was prepared in a similar way, but with chlorine instead of bromine. The product was a similar, white and light material, with low solubility in carbon tetrachloride and cyclohexane.

Microscopical examinations showed no distinct crystals. The materials turned dark at about 140°C and charred later without melting and without visible evolution of bromine or chlorine gas. Hexabromoethane decomposes at 210–215°C and gives off free bromine. Infrared spectra of the two samples showed the materials to be high-symmetric, saturated,

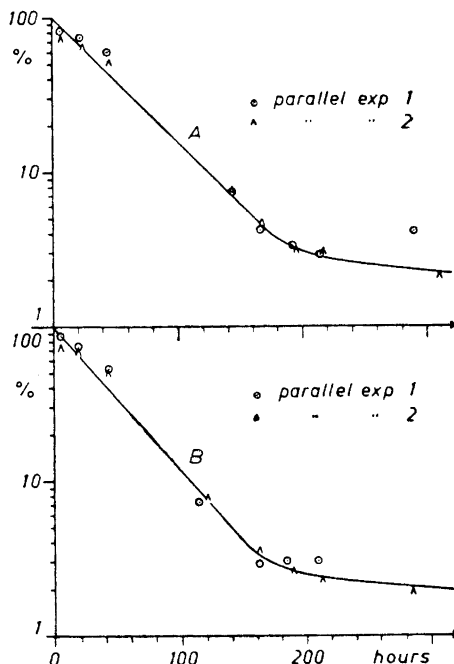


Fig. 2. Activity in organic phase as percentage of activity at zero time.

Curve A: $[C_2Br_6^*] = 1.24$ mmole/l,
 $[Br_2^*] = 28.2$ mmole/l.
 Curve B: $[C_2Br_6^*] = 1.24$ mmole/l,
 $[Br_2^*] = 0.58$ mmole/l.

containing C–C bonds and to a small extent C–Br and C–Cl bonds, respectively. In the case of chlorine this has consequently exchanged with the organic bound bromine. There were no oxides, no C–H bonds and no functional groups.

To study the reaction without complications from the exchange reaction, hexabromoethane and free bromine were irradiated in the pile in two different ampoules placed in the same container to get the same specific activities. Different series of measurements with different concentrations of free bromine were carried out.[†]

Fig. 2 shows two typical runs at 20°C in nitrogen atmosphere for two different bromine concentrations. In either case, two parallel experiments were carried out.

Fig. 2 shows that the reactions are represented by nearly straight lines on a semi-logarithmic scale. The slopes seem

nearly independent of the amount of free bromine in this region of concentration.

Runs with free iodine instead of bromine or chlorine gave no reaction.

An experiment with symmetric tetrabromethane and free chlorine gave a marked reaction. A yellow, viscous oil was isolated.

A rough test with radioactive free chlorine and inactive hexabromoethane showed an uptake of chlorine activity in the organic phase, later falling off again.

The curves, Fig. 2, show that the organic bound activities fall to at least 2% of the original activities. Setting aside isotope effect, this may indicate a polymer consisting of some system of condensed carbon rings.

Further investigations are in progress.

1. Seely, L. B., Jr. and Willard, J. E. *J. Am. Chem. Soc.* **69** (1947) 2061.
2. Mouneyrat, X. *Bull. soc. chim.* **19** (1898) 177.
3. Dickinson, R. G. and Leermakers, J. A. *J. Am. Chem. Soc.* **54** (1932) 3853.

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The Precipitation of Neutral Polysaccharides by Cationic Detergents

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During an investigation on the charged polysaccharide luteic acid, described by Raistrick and collaborators in 1931¹, the method of Scott was used as one step in the purification of it. It has been shown² that it is possible to use detergents for the precipitation and separation of mixtures of charged polysaccharides (and desoxyribonucleic acid). For obvious reasons neutral polysaccharides cannot be precipitated directly by the use of detergents such as cetylpyridinium chloride (C.P.C.) or cetyltrimethylammonium bromide (C.T.A.B.). If, however, the neutral polysaccharide is

coupled to borate and C.P.C. is added, complete precipitation can be achieved. Since the work in this paper was carried out a short communication has appeared also recording this fact³. The precipitates are soluble in salt solutions, dilute acids and glycerol and galactose solutions.

To eliminate the effect of buffer salts on the precipitate, cetyltrimethyl ammonium borate (C.T.A. Borate) was prepared and used as the precipitant. The pH dependence of the reaction was marked, as was observed by Barker *et al.*³ Rat liver glycogen was not precipitated by C.T.A. borate, which had a pH of 8.5, but the addition of a few drops of ammonia resulted in good precipitation. Yeast mannan and ivory nut mannan were precipitated immediately without the addition of ammonia. Inulin, dextran and starch were not precipitated even in the presence of ammonia, but only on adding an appreciable concentration of potassium hydroxide. This latter type of precipitation in potassium hydroxide also took place in the absence of borate, and although the precipitates were soluble in salt solutions they were resistant to solvent action by glycerol or galactose.

It is therefore clear that there are two possibilities of precipitating neutral polysaccharides with amphipathic cations, due to the acquiring of polyanionic properties:

- (1) by formation of borate complexes, and
- (2) by the ionisation of hydroxyl groups at high pH.

The possibility of salt fractionation, such as is available with acidic polysaccharides², coupled with the differential solubilities of the precipitates in glycerol and galactose solutions, suggest that this reaction has great potential practical value. The following experiment describes a simple test of its utility (see also Barker *et al.*³).

The test system used was glycogen from *Escherichia coli* B alone or in combination with luteic acid. It was possible to separate these polysaccharides by precipitating the luteic acid directly with C.P.C. The glycogen was then precipitated by making the solution 0.01 M with regard to borate, adjusting the pH to 9.2 with KOH and finally adding C.P.C. to complete precipitation. This last operation should be finished within an hour, since the solution may otherwise be discoloured due to slight decomposition of C.P.C. in alkaline solutions. The supernatant contained hardly detectable amounts of polysaccharide.

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