

with external cooling with tap water. The stirring was continued for 6 h, then the solution was filtered. The silver salts were washed with some dimethylformamide and, after chloroform (100 ml) had been added to the combined filtrate and washings, the solution was washed with 6% aqueous potassium cyanide (100 ml). After washing the aqueous phase with chloroform (2 × 25 ml), the chloroform layers were combined and were washed with water (2 × 50 ml), dried over calcium chloride and concentrated. The remaining dimethylformamide was removed by co-distillation with butanol. The crystalline residue was recrystallised from ethanol, and this, together with the material obtained by working up the mother liquors, gave a total of 1.90 g having m.p. 104–105°. After further crystallisations the product had m.p. 110–111° (corr.) and $[\alpha]_D^{25} -35^\circ$ ($c = 1$, in chloroform).

Methyl 4-O-methyl-β-D-glucopyranoside. By deacetylation of the above acetate the glycoside was obtained. After crystallisation from ethyl acetate it had m.p. 102–103° (corr.), $[\alpha]_D^{20} -18^\circ$ ($c = 1$, in water).

4-O-Methyl-D-glucose. Acid hydrolysis of the glycoside yielded 4-O-methyl-D-glucose. $R_{\text{Glucose}} 2.40$ (in butanol-ethanol-water, 10:3:5). $M_G 0.17$ (in 0.1 M borate buffer of pH 10). The corresponding values for 2-, 3- and 6-O-methyl-D-glucose were $R_{\text{Glucose}} 2.78, 2.67$ and 2.47 and $M_G, 0.17, 0.80$ and 0.75 , respectively.

The authors are indebted to Professor J. K. N. Jones for a gift of 4-O-methyl-D-glucose.

1. Bourne, E. J. and Peat, S. *Advances in Carbohydrate Chem.* **5** (1950) 145.
2. Mc Gilvray, D. I. *J. Chem. Soc.* **1952** 3648.
3. Gorin, P. A. J. *Can. J. Chem.* **35** (1957) 595.
4. Haworth, W. N., Hirst, E. L. and Teece, E. G. *J. Chem. Soc.* **1931** 2858.
5. Helferich, B. and Lang, O. *J. prakt. Chem.* **132** (1932) 321.
6. Kuhn, R., Trischmann, H. and Löw, I. *Angew. Chem.* **67** (1955) 32.

Received December 6, 1957.

Preliminary Calculations of Mean Amplitudes of Vibration in Cyclopropane

O. BASTIANSEN and S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

Reinvestigations on the structures of the *cycloalkanes* are in progress¹. From the radial distribution curve of *cyclopropane* the root mean square amplitude of vibration (u) has been calculated for the C—H and C—C bond distances. Least square calculations were applied to fit Gaussian shaped peaks to the peaks of the radial distribution curve. It was observed that there was a reproducible deviation from the symmetric form due to anharmonicity^{2,3}. However, this effect will not be discussed here. The electron diffraction results for values of u are listed in Table 1.

Table 1. Mean amplitudes of vibration in *cyclopropane* (Å units).

Distance	El.diff.	Spectr.
C—H	0.0784 ± 0.0015	0.0770
C—C	0.0480 ± 0.0015	0.0489

It is of interest to compare these values with theoretical ones calculated from spectroscopic data. Some simple, approximate methods, which yield data of sufficient accuracy for this purpose, shall be reported in this communication.

The C—H distances. The four C—H stretching fundamental frequencies have been separated from the remaining fundamentals. Thus an explicit approximate formula for the mean square amplitude could be evaluated, the result being⁴

$$u_{\text{C-H}}^2 = h (\mu_{\text{H}} + \mu_{\text{C}})^{1/2} / 4\pi k^{1/2}$$

where only the principal C—H stretching force constant (k) appears. μ_{H} and μ_{C} are the inverse masses of the H and C atoms. From the experimental fundamentals⁵ (A_1') 3 029, (E') 3 024.4, (A_1'') 3 103.0 and (E'') 3 080 cm^{-1} , the value

$k = 5.120 \times 10^5$ 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.

Received October 31, 1957.

A Photoactivated Polymerization of Hexabromoethane

K. TAUGBØL and J. B. DAHL

Joint Establishment for Nuclear Energy Research, Kjeller, Norway

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

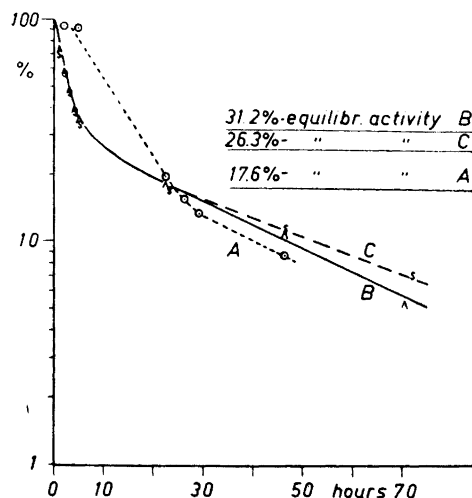


Fig. 1. Activity in organic phase as percentage of activity at zero time.

- 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-