Lattice Frequencies of Benzene Crystal

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Hence, the rate of formation of HBr measures the rate of the initial dissociation of the molecule RBr. Assuming that the recombination process

$$R + Br \rightarrow RBr$$
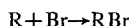
does not require any activation energy, we consider that the C−Br bond dissociation energy is equal to the activation energy of process (1).

We have recently applied this technique for the determination of the C−Br bond dissociation energies in polyhalogenated bromomethanes, and report here the results obtained for trichlorobromomethane. The evidence of present experiments leaves no doubt that the dissociation takes place according to the equation

$$Cl_3CBr \rightarrow Cl_3C \cdot + Br.$$

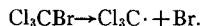Hydrogen bromide* was formed in the pyrolysis. Moreover, the formation of dibenzyl is further proof that the dissociation process involves a radical split of the Cl_3CBr molecule. In accordance with the mechanism outlined above the rate of decomposition was measured by the rate of formation of HBr, and we found that the reaction obeys first-order kinetics. The unimolecular rate constant was not affected by the variation of the partial pressure of Cl_3CBr by a factor of 4.5 (from 0.18 to 0.83 mm Hg) and of the time of contact by a factor of 4 (from 0.3 to 1.3 sec.). The rate constant remained also independent of the pressure of toluene when the latter was varied by a factor of 2 (from 10 to 21 mm Hg). The plot of the unimolecular rate constant against $1/T$ is shown in Fig. 1. The straight line corresponds to an activation energy of 48 ± 1 kcal./mole and to a frequency factor of 1.10^{13} sec.$^{-1}$. The latter value is considered to be an additional proof for the unimolecularity of the dissociation process (1).

Making the usual assumption that the recombination process
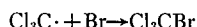
$$Cl_3C \cdot + Br \rightarrow Cl_3CBr$$

does not require any activation energy, we conclude that the C−Br bond dissociation energy in trichlorobromomethane is 48 ± 1 kcal./mole.† Three values for $D(Cl_3C-Br)$ can be deduced from investigations of other workers. The study of the photo-oxidation of trichlorobromomethane by Franke and Schumacher[3] leads to a value of about 45 kcal./mole. The studies of bromine exchange reactions makes it possible to estimate the activation energy of the reaction $Cl_3CBr + Br \rightarrow Cl_3C \cdot + Br_2$; and the results obtained by Miller and Willard[4] lead to $D(Cl_3C-Br) < 52$ kcal./mole, while those reported by Davidson and Sullivan[5] to $D(Cl_3C-Br) < 57$ kcal./mole.

The striking point emerging from these studies is the great difference between $D(CH_3-Br)$ and $D(CCl_3-Br)$. For the former bond dissociation energy a value of 68–69 kcal./mole can be deduced on basis of existing thermochemical data and of the known value for $D(CH_3-H)$. Our investigation of the pyrolysis of methyl bromide indicates that $D(CH_3-Br) \approx 67$ kcal./mole. The C−Br bond dissociation energy in trichlorobromomethane is, therefore, lower by about 20 kcal./mole than in methyl bromide. It seems that this decrease is to be attributed mainly to the steric repulsion between the bulky chlorine and bromine atoms in the Cl_3CBr molecule, since our preliminary studies of the pyrolysis of trifluorobromomethane suggests that the difference $D(CH_3-Br) - D(CF_3-Br)$ is about 4 kcal./mole only.

In our opinion two factors contribute to the steric effect responsible for the weakening of the C−Br bond in Cl_3CBr. The strain due to the interaction of the bulky chlorine atoms in any molecule Cl_3CX is released when the molecule dissociates and a planar $Cl_3C \cdot$ radical is formed (see e.g. Brown[6] and Szwarc[7]). This factor is responsible for the known stability of the Cl_3C radical.[8] In the particular case of Cl_3CBr the additional decrease in the C−Br bond strength is due to the bulkiness of the bromine atom. The latter effect becomes evident on comparing the difference $D(CH_3-Br) - D(CCl_3-Br) \approx 20$ kcal./mole, with the difference $D(CH_3-H) - D(CCl_3-H)‡$ which is equal to about 12 kcal./mole only.

A full account of the determination of C−Br bond dissociation energies in polyhalogenated bromomethanes is in course of preparation.

* It was shown that no HCl was produced within the temperature range used for the thermal decomposition of Cl_3CBr, i.e., 718–827°K.
† If, however, some activation energy were required for the recombination process, the $D(CCl_3-Br)$ would be even smaller than 48 kcal./mole.
‡ $D(CCl_3-H)$ is estimated at about 89 kcal./mole from the data of Schumacher et al. See H. J. Schumacher and K. Wolf, Zeits. f. physik Chemie B25, 161 (1934); J. V. Braunwarth and H. J. Schumacher, Kolloid Zeits. 89, 184 (1939).

[1] M. Szwarc and B. N. Ghosh, J. Chem. Phys. 17, 744 (1949).
[2] Szwarc, Ghosh, and Sehon, J. Chem. Phys. (to be published).
[3] W. Francke and H. J. Schumacker, Zeits. f. physik. Chemie B.42, 297 (1939).
[4] A. A. Miller and J. E. Willard, J. Chem. Phys. 17, 168 (1949).
[5] N. Davidson and J. H. Sullivan, J. Chem. Phys. 17, 176 (1949).
[6] H. C. Brown, et al., J. Am. Chem. Soc. 67, 378 (1945) and following papers.
[7] M. Szwarc, Disc. Faraday Soc. 2, 39 (1947).
[8] M. S. Kharash et al., J. Am. Chem. Soc. 69, 1100, 1105 (1947).

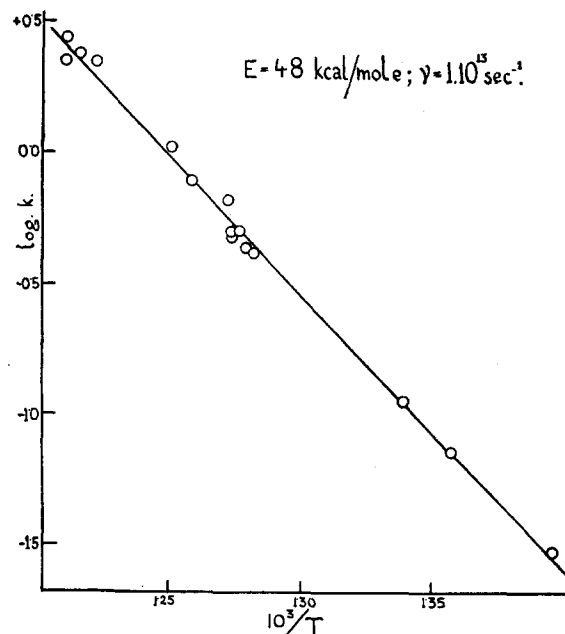$E = 48$ kcal/mole; $\nu = 1.10^{13}$ sec^{-1}.

FIG. 1.

Lattice Frequencies of Benzene Crystal

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FROM the polarization characteristics of the Raman lines of crystalline benzene Fruhling[1] has recently reported in this journal that the 63 (ν_2) and 105 cm^{-1} (ν_4) lines arise from the rotational oscillations about the two axes of inertia situated in the plane of the molecule (hereafter designated as I) and that the 35 (ν_1) and 69 cm^{-1} (ν_3) lines arise from those about the hexagonal axis (hereafter designated as II).

Although the assignment of these lines is not discussed in detail in his paper, the conclusion does not seem to be reconcilable with the Raman measurements recently made by one of us (I.I.) from −10° down to −190°C. In this temperature range all these lines change their frequencies linearly with the absolute temperature T: $\nu_1 = 69 - 0.100T$, $\nu_2 = 89 - 0.083T$, $\nu_3 = 112 - 0.127T$, $\nu_4 = 141 - 0.128T$ cm^{-1}.

The ν_4-line has almost the same intensity as the ν_2-line at lower temperatures but the former becomes more diffuse and weaker

than the latter at higher temperatures, so that these two lines cannot be considered to arise from the same kind of molecular motion. An examination of the lattice structure[2] suggests that the energy required for the rotation or tunneling of benzene molecules about their hexagonal axes would be much less than that for the rotation about the axes in the molecular plane. Such motions would considerably affect the potential field described in our previous paper[3] and in consequence the corresponding Raman lines would become diffuse. Since the tunneling or the non-uniform rotation about the hexagonal axes occurs very probably at higher temperatures,[4] it seems more reasonable to assign ν_4 to II rather than to I.

If such an argument be admitted, we cannot assign ν_1 to II, since the intensity of this line increases with rising temperature. The fact that the intensity of ν_1 is very weak at low temperatures might suggest that this frequency corresponds to a forbidden line to be assigned to a translational vibration which tends to appear in the Raman effect at higher temperatures. (The potential field in the benzene crystal has a center of symmetry and, there-fore, all the translational oscillations are forbidden in the Raman effect.[3] The large anharmonicity in the molecular oscillation in the lattice which would give rise to the considerable temperature dependence of the lattice frequencies would also be responsible for the appearance of the forbidden Raman lines at higher temperatures.)[5]

This conclusion would be supported by our experimental result on the Raman effect of pyridine crystal whose potential field has no center of symmetry and which would, therefore, show the Raman lines of the translational oscillation. At $-190°C$ we found four lattice frequencies in the Raman effect which are practically equal to those of the crystalline benzene at the same temperature and the lowest frequency (ν_1) was found to be considerably stronger in intensity than that of benzene.

[1] A. Fruhling, J. Chem. Phys. 18, 1119 (1950).
[2] E. G. Cox, Proc. Roy. Soc. A135, 491 (1932).
[3] I. Ichishima and S. Mizushima, J. Chem. Phys. 18, 1420 (1950).
[4] E. R. Andrew, J. Chem. Phys. 18, 607 (1950).
[5] In this connection we want to point out the strong distortions of the ellipsoid of polarizabilities due to the large mobility of the π-electrons which was already reported by Fruhling (see reference 1).

Errata: The Photo-Chemical Reduction of Water by Europium (II) Ion, and the Magnetic Susceptibilities of Europium (II) and Europium (III) Ions

[J. Chem. Phys. 17, 1345 (1949)]

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AN error has been found in the calculation of the quantum yields tabulated in Table I. The numbers of quanta ab-sorbed should be, reading from top to bottom: 34.0×10^{19}, 31.2×10^{19}, 27.7×10^{19}, and 29.7×10^{19}. The corresponding corrected values of the quantum yield are: 0.15 ± 0.02, 0.16 ± 0.02, 0.18 ± 0.02, and 0.20 ± 0.02.