

Determination of the Dissociation Energy of the C–Br Bond by Pyrolysis

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TABLE I.

pH	c (g/liter)	i_{90}/KMc	i_{45}/i_{135}	d_{ψ}	d_z	d_m
3.12	0.161	0.695	0.890	380A	590A	900A
	0.294	0.605	0.865	335	540	735
	0.408	0.500	0.845	325	460	660
3.20	0.690	0.485	0.830	275	470	555
	1.15	0.388	0.830	250	380	465
3.29	1.72	0.300	0.835	225	300	410
	1.87	0.280	0.870	225	240	395
	2.19	0.255	0.890	210	230	375
	2.62	0.230	0.910	200	180	355
	3.28	0.215	0.935	185	160	330
	7.00	0.164	1.00	82	—	255

Corrections for this effect would lead to somewhat larger values; however, this first approximation is entered in the table as d_z . On the other hand, the value of d' as defined by the hard sphere approximation is obtained at once by fitting the dissymmetry data to the foregoing equation. These values of d are entered in the table as d_z , and as anticipated are seen to be generally larger than d_{ψ} . As a reference, the mean intermolecular distance d_m is given in the last column: this represents the upper limit to which d could approach. It thus appears that an approximate means has been found to represent the distribution of charged macromolecules in solution in addition to explaining the unusual light scattering data.

As expected the addition of a salt greatly diminishes these effects: both i/KMc and the dissymmetry approach unity at molalities of a few thousandths. When the dissymmetry has become unity, the downward curvature of the plot of Kc/i (or Hc/r) against c disappears and the conditions required for the application of the fluctuation theory seem to be reinstated.

It is of interest to notice that if the value of d were of the order of thousands of Angstroms rather than hundreds and if the scattering could be observed at much lower concentrations the appearance of maxima in the angular intensity data would be expected. In this event it would then be practical to carry out a Fourier inversion and so arrive for the first time at the detailed radial distribution of charged macromolecules in solution. Solutions of some virus molecules provide these conditions and the possibilities thus offered are being explored.

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² P. Debye, Physik. Zeits. 28, 135 (1927).

Exchange of Ions between the Surface of Crystals and Solutions

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June 20, 1949

THE exchange of ions between the surfaces of crystals and solutions has been used as the basis for a radioactive method for determining the active surface area of a precipitate.¹ While the active surface area is not necessarily the same as the geometric surface area, there is no doubt that the active surface area, as measured by exchange, is a characteristic property of the crystals which could be of considerable interest and importance.

In the so called, direct method, the exchange is measured with the help of a radioactive ion, isotopic with one of those in the precipitate and it should, in principle, be possible to use either the anion or the cation, or both, as tracers. We have now used both anion and cation to measure the area of crystals of strontium sulphate. The crystals, prepared by the addition of excess sulphuric acid to strontium chloride solution, were washed repeatedly with water and then aged for two years in contact with saturated strontium sulphate solution at room temperature.

Using a shaking time of ten minutes:

Active area, using $^{90}\text{Sr}^{++}$, = 14.9×10^3 sq. cm per gram;²

Active area, using $^{35}\text{SO}_4^{--}$, = 8.3×10^3 sq. cm per gram.³

The over-all precision of the measurements is thought to be about 4 percent.

The difference in areas as measured by Sr^{90} and S^{35} is quite beyond the limits of experimental error and would seem to be of considerable interest. It may be connected with the fact that excess sulphuric acid was used in preparing the strontium sulphate and experiments are being carried out to test this point. Alternatively, it may be related to the differing radii of the ions and to differing surface activity coefficients (see Coryell in reference 1.)

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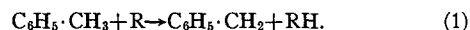
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Determination of the Dissociation Energy of the C—Br Bond by Pyrolysis

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June 27, 1949

AN estimation of the dissociation energies of the C—Br bonds of various organic bromides should be of great interest, since knowledge of these dissociation energies, combined with the heats of formation of the relevant bromides in the gaseous state, makes it possible to determine the heats of formation of various organic radicals, and subsequently to calculate the various C—H dissociation energies, the resonance energies of these radicals, and related quantities.

The C—Br dissociation energy of an organic bromide can be estimated by investigating its pyrolysis in a stream of toluene used as a carrier gas. It was shown in previous communications that toluene is very effective in removing various radicals¹ which react with it according to Eq. (1).



Benzyl radicals produced in this process dimerise, forming dibenzyl which appears as one of the products of pyrolysis.

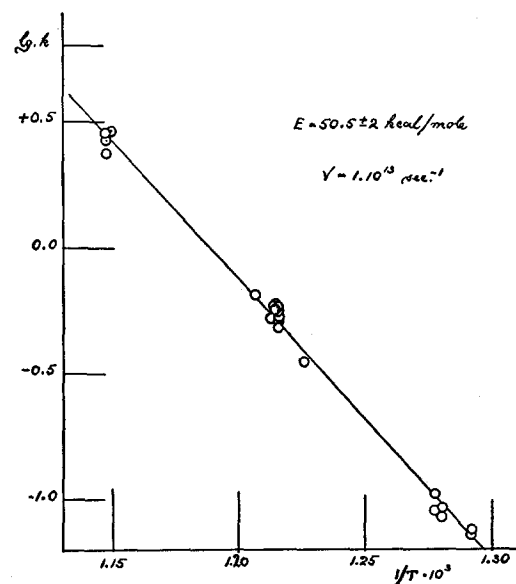


FIG. 1. Benzyl bromide.

We might expect that pyrolysis of an organic bromide RBr would result in a splitting of its molecule into a radical R and a Br atom. If toluene is used as a carrier gas then both fragments can react with it, and according to Eq. (1) each decomposed molecule of RBr would produce one molecule of HBr , one of RH and one of dibenzyl. Therefore, if this scheme applies, the rate of decomposition of bromide might be measured by the rate of formation of HBr , RH , or dibenzyl.

It is possible, however, that a molecule of organic bromide would decompose into HBr and the corresponding olefin.² This case can be easily distinguished from the former one, for although HBr would again be a product of pyrolysis, no dibenzyl would be produced. Hence, using toluene as a carrier gas one should be able to measure for an organic bromide both the rate of decomposition into radicals according to Eq. (2)



and into HBr and olefin according to Eq. (3)



even if these reactions occur simultaneously. The rate of reaction (2) would be measured by the rate of formation of dibenzyl, while the sum of the rates of both reactions (2) and (3) would be measured by the rate of formation of HBr .

Having described in general terms the principles of our method of pyrolysis of organic bromides we report now briefly the results obtained for benzyl bromide and allyl bromide. The apparatus used for these investigations as well as the experimental technique have been described previously.^{1a,16} An extra liquid air trap to collect the HBr was added before the first mercury vapor pump.

The rate of decomposition of benzyl bromide was measured by the rate of formation of either HBr or dibenzyl. It was shown that, within the experimental error, the molar ratio of dibenzyl to HBr was 1:1. Variation of the partial pressure of benzyl bromide (by a factor of 200) and of the time of contact (by a factor 3) demonstrated that the kinetics of the decomposition obeyed a first-order law. Variation of the partial pressure of toluene proved that the rate of decomposition of benzyl bromide was independent of the toluene pressure. Plot of the \lg of unimolecular rate constant against $1/T$ for the temperature range 500°C to 600°C is shown in Fig. 1. The straight line corresponds to an activation energy of 50.5 ± 2 kcal/mole and a frequency factor of 1.10^{13} sec.⁻¹. The numerical value of the latter is an indication that the decomposition is indeed a unimolecular process.

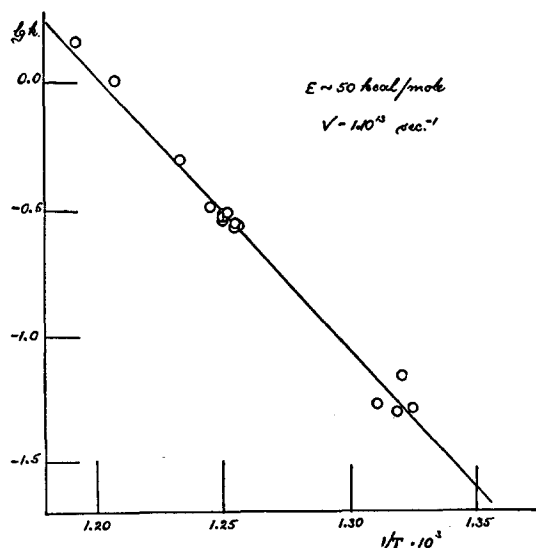


FIG. 2. Allyl bromide.

Assuming that the recombination of benzyl radicals and bromine atoms does not involve any activation energy, we conclude that the dissociation energy of the $C-Br$ bond in benzyl-bromide is equal to the observed activation energy of the decomposition process, i.e., to 50.5 ± 2 kcal/mole. This conclusion may be checked in the following way. The dissociation energy of the $C-H$ bond in toluene was determined at 77.5 ± 1.3 kcal/mole.³ The difference between this dissociation energy and that of the $C-Br$ bond in benzyl bromide was estimated calorimetrically at 29 ± 3 kcal,⁴ while the dissociation energies directly estimated by pyrolysis differ by 27 ± 3.3 kcal. We see, therefore, that the agreement is very satisfactory.

A similar study of the pyrolysis of allyl-bromide leads to a value of about 50 kcal/mole for the dissociation energy of the $C-Br$ bond in this compound. The plot of $\lg k$ against $1/T$ is given in Fig. 2. The kinetics of the decomposition of allyl-bromide shows some peculiarities. The allyl radical, being very stable (probably as stable as the benzyl radical), does not react only with toluene but partially dimerises or associates with benzyl radicals. Therefore, the amount of dibenzyl formed in the pyrolysis of allyl-bromide is much lower than the amount of HBr , and it cannot be taken as a measure of decomposition.

A full account of these investigations is in course of publication.

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² See, for example, E. T. Lessig, *J. Phys. Chem.* **36**, 2335 (1932); E. L. Vernon and F. Daniels, *J. Am. Chem. Soc.* **55**, 922 (1933); P. Fugassi and F. Daniels, *J. Am. Chem. Soc.* **60**, 771 (1938); F. Daniels and P. L. Veltman, *J. Chem. Phys.* **7**, 756 (1939).

³ M. Szwarc, *Nature* **160**, 403 (1947); *J. Chem. Phys.* **16**, 128 (1948).

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Anomalous Mobility of H^+ and OH^- Ions

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THE mobility of H^+ and OH^- ions in water is much higher than that of other ions; its dependency on temperature and pressure is anomalous. If we assume that these ions are small complex hydrates, e.g., H_3O^+ , we may expect mobilities of usual magnitude which are comparable to those of the Na^+ and Cl^- ions. Hence we may define excess mobilities $u^+ = u_{H^+} - u_{Na^+}$ and $u^- = u_{OH^-} - u_{Cl^-}$ due to special elementary processes. We postulate that these elementary processes behave "normally," i.e., that the dependence of their number per second (frequency) on temperature is of the form $\text{const.} \exp(-q/kT)$. The deviations of u^+ and u^- from this dependence on temperature are supposed to be due to structural changes of the water and will be taken into account by means of a factor $f(T)$.

So we put $u^+ = u_0^+ \cdot f^+(T) \cdot \exp(-q^+/kT)$ and $u^- = u_0^- \cdot f^-(T) \cdot \exp(-q^-/kT)$; the factor $f(T)$ is to be determined independently.

Eucken¹ tentatively expressed the anomalies of the volume and the specific heat of water by introducing mole fractions $\gamma_1, \gamma_2, \gamma_3, \gamma_4$ of different forms of association of water, γ_4 referring to the association form of larger volume, like ice. Eucken supposes that these association forms are cyclic ones.

We find that $f(T)$ can be derived from these values of γ_i when we assume that the icy association forms do not participate in the excess conductivity. We obtain the result that $f(T)$ means the number of H bridges per molecule H_2O in the non-icy association forms according to the formula $f^+(T) = f^-(T) = \frac{1}{2}\gamma_2 + \frac{1}{3}\gamma_3$ (see Table I). Also u_0 is equal for the H^+ and the OH^- ions. From the quotients $u^+/f(T)$ and $u^-/f(T)$ we obtain $q^+ = 2.4$ kcal/mole and $q^- = 3.0$ kcal/mole, both values being constant between 0° and 306°C . The value of u_0 can be calculated according to the theories of exchange of places.²