

By use of data on the Kerr constant and depolarisation factor, the mean polarisability of a bond can be resolved into polarisabilities in directions along and at right angles to the bond. These quantities also are characteristic of the bond and the longitudinal polarisability especially is closely related to its length and order. In diatomic hydrides, the longitudinal polarisability of the bond is proportional to the third power of the bond length, whilst in the case of bonds not involving hydrogen, the longitudinal polarisability is given approximately by $b_l \times 10^{23} = n^2 r^3 + 6.0$, where n is the bond order and r its length in Ångströms.

*The Chemistry Department,
The University College, Southampton.*

THE KINETICS OF THE DECOMPOSITION OF BENZENE DIAZONIUM CHLORIDE IN WATER.

BY E. A. MOELWYN-HUGHES AND P. JOHNSON.

Received 17th June, 1940.

The variation of the unimolecular velocity coefficient, k , with respect to temperature, T , is usually expressed by

$$\frac{d \ln k}{dT} = \frac{E_A}{RT^2} \quad (1)$$

where E_A is the apparent energy of activation. For the majority of reactions which have been studied, E_A is seemingly constant within the explored temperature range. Before a true constancy of E_A can be established, however, more accurate values of k are required, and a more extensive range of temperature must be covered. A number of catalysed and uncatalysed unimolecular reactions examined during recent years have been found, in fact, to possess an apparent energy of activation which varies with the temperature. As a first approximation, the variation is adequately expressed by the linear equation

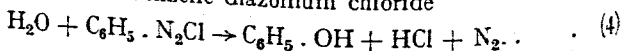
$$E_A = E + JT \quad (2)$$

where J is a specific constant. The integrated expression for temperature variation is consequently

$$\ln k = C + (J/R) \ln T - \frac{E}{RT} \quad (3)$$

The reactions which have been shown to conform more closely to equation (3) than to the Arrhenius equation ($\ln k = B - A/RT$) include the following: hydrogen-ion catalysed hydrolysis of glykosides; uncatalysed hydrolysis of the alkyl halides; elimination of CO_2 from aqueous solutions of carboxylic acids; mutarotations of pentoses, hexoses and reducing disaccharides in water.¹

In the present paper, we give the results obtained for the kinetics of the decomposition of benzene diazonium chloride



¹ Moelwyn-Hughes, *Proc. Roy. Soc., A.*, 1938, 164, 295. Johnson and Moelwyn-Hughes, *ibid.*, 1940, 175, 118. Kendrew and Moelwyn-Hughes, *ibid.*, in the press.

Two independent methods of analysis, which are described later, lead to values of -38 and -32 for J . In round figures we therefore take J/R to be -18 . Table I is a summary of our experimental results, in which the units are reciprocal seconds, calories per g.-molecule, and seconds respectively for k , E_A , and half-life, $t_{1/2}$.

TABLE I.

| Temperature. | k . | E_A . | $t_{1/2}$. |
|--------------|-----------------------|---------|-------------|
| 283.16 | 9.30×10^{-6} | 27923 | 74540 |
| 333.17 | 5.64×10^{-3} | 26122 | 122.9 |

$J/R = -18.0 \pm 1.5.$

Experimental.

Much work on the kinetics of the decomposition of benzene diazonium chloride in aqueous solution has already been done.² In some of this no isolation of the solid compound was attempted, the kinetic measurements being carried out on material of doubtful purity. Nor were precautions taken to prevent supersaturation of the solutions in the manometric method employed. The accumulated data from all workers in this field is neither sufficiently extensive nor precise to allow an evaluation of J .

In the work described here, the solid compound was isolated and washed. The decomposition was studied by a manometric method, in which difficulties due to supersaturation of the solution by the nitrogen evolved were removed.

The preparation of solid diazobenzene chloride was based on the method of Pray,³ whose quantities were found suitable. The rate of addition of aniline hydrochloride to the suspension of amyl nitrite to the suspension of aniline hydrochloride in glacial acetic acid was such that the temperature of the mixture did not fall below 273°K . or rise above 283°K . Diazotisation was allowed to proceed within these temperature limits for a further two hours. The addition of ether to precipitate the solid occupied a further two hours. The solid was stored under ether in a desiccator.

The manometer employed is a modification of the Barcroft apparatus, designed to allow the measurement of fast reaction rates as well as of moderately slow ones. Accurate kinetic data were obtained over a range of 45° , and slightly less accurate

values outside this range. The method allowed the addition of foreign substances (even of high vapour pressure), no elaborate system of correction being thereby necessary. The two arms of a xylene manometer of height 30 cm., constructed of capillary tubing, were connected to equal height 600 c.c. pyrex flasks A and A' by lengths of glass tubing XB and X'B' provided with "T" pieces and good vacuum taps T and T', and lengths of good quality rubber pressure tubing R and R' (Fig. 1).

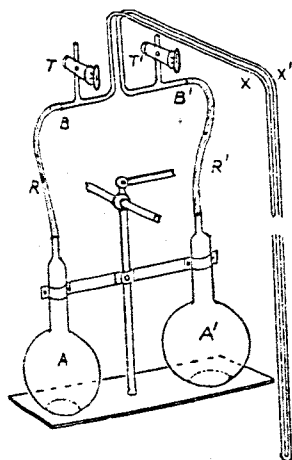


FIG. 1.

² E.g., Cain and Nicoll, *J.C.S.*, 1902, 81, 1412.

³ Pray, *J. Physical Chem.*, 1926, 30, 1473.