

The Effect of Pressure up to 12,000 kg/cm² on Reactions in Solution

By E. G. WILLIAMS, M. W. PERRIN, and R. O. GIBSON

(Communicated by C. N. Hinshelwood, F.R.S.—Received December 17, 1935)

INTRODUCTION

In a previous publication* it was shown that pressure was capable of exerting a considerable influence on the rate of reactions in solution. Two reactions were studied; the first, the interaction of sodium ethoxide and ethyl iodide in alcohol solution, was a typical example of the "normal" class, in which the number of molecules reacting is approximately equal to the number of collisions with the requisite activation energy, while the second, the interaction of pyridine and ethyl iodide in acetone solution, was a typical "slow" reaction, in which the number of molecules reacting is several powers of 10 less than the number of collisions with the requisite activation energy. The rates of both reactions were increased by pressure, but while the first was accelerated 1.6 times at 3000 kg/cm², the second was accelerated 7.2 times at 3000 kg/cm², and much more at higher pressures.

It seemed desirable to investigate other reactions falling into these two classes, to see whether this behaviour was general. With this end in view, the hydrolysis of sodium monochloracetate by aqueous caustic soda, another typical "normal" reaction, has been studied up to 12,000 kg/cm², and the work on the sodium ethoxide and ethyl iodide reaction has also been extended to this pressure.

The esterification of acetic anhydride by ethyl alcohol was selected as another typical "slow" reaction, and has been studied up to 3000 kg/cm² in various solvents, and up to 8500 kg/cm² in toluene.

In addition, the unimolecular decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform solution, has been studied up to 3000 kg/cm².

In each case the temperature coefficients of the reactions have been measured, in an attempt to show whether the change in the velocity constant K is due to a change in the constant A or the constant E in the Arrhenius equation, $K = Ae^{-E/RT}$.

The results are given below, with brief comments, and are discussed more fully as a whole, at the end of the paper.

* Gibson, Fawcett, and Perrin, 'Proc. Roy. Soc.,' A, vol. 150, p. 223 (1935).

APPARATUS

This consisted of the 3000 kg/cm² sampling bomb, and the special 12,000 kg/cm² apparatus both of which have been fully described previously.*

SODIUM ETHOXIDE AND ETHYL IODIDE IN ALCOHOL

The work* up to 3000 kg/cm² has now been extended to 12,000 kg/cm². The materials used were the same as before. The reaction could not be studied below 25° C at 12,000 kg/cm², as mercury freezes at 22° C at this pressure. The values at the higher pressures were not very reliable, as the individual constants sometimes differed by as much as 30% from the mean.

TABLE I—SODIUM ETHOXIDE AND ETHYL IODIDE IN ALCOHOL SOLUTION

Temperature ° C	Pressure kg/cm ²	$K' \times 10^3$	$K \text{ (obs.)}$ $\times 10^3$	$K \text{ (calc.)}$ $\times 10^3$
14.85	1	—	2.30	2.27
19.95	1	—	4.19	4.26
25.0	1	—	7.73	7.79
30.0	1	—	13.6	13.9
14.85	2980	4.23	3.65	3.57
19.95	2980	7.59	6.53	6.72
25.0	2980	14.4	12.4	12.3
30.0	2980	25.2	21.6	22.0
15.0	5000	5.6	4.6	4.65
20.0	5000	10.3	8.4	8.48
25.1	5000	19.4	15.9	15.8
30.1	5000	34.2	28.1	27.5
15.1	8500	6.1	4.7	—
20.0	8500	13.5	10.5	—
25.1	8500	22.0	17.1	—
30.1	8500	43.4	33.8	—
25.2	12,000	25.2	18.6	—
30.1	12,000	52.5	38.8	—

The results are given in Table I, with those from the previous work included for comparison. Column 3 shows the constants (K') uncorrected for the changes in concentration due to the thermal expansion and compressibility of the solvent, and column 4 (K_{obs}) the corrected values. The solutions were 0.1 normal, and the constants are given in terms of gram mol/litre/minute.

* Gibson, Fawcett, and Perrin, 'Proc. Roy. Soc.,' A, vol. 150, p. 223 (1935).

The velocity is seen to increase with pressure, but the effect is not very marked, and the rate at 12,000 kg/cm² is still only rather less than three times that at atmospheric pressure.

Values of E and A , the constants of the Arrhenius equation, have been calculated for the 5000 kg/cm² results and are given below, with the results from the previous work for 1 and 3000 kg/cm²:

$$\text{for } 1 \text{ kg/cm}^2 \text{ } K = 1.28 \times 10^{13} e^{-20,740/RT}$$

$$\text{for } 3000 \text{ kg/cm}^2 \text{ } K = 2.23 \times 10^{13} e^{-20,800/RT}$$

$$\text{for } 5000 \text{ kg/cm}^2 \text{ } K = 1.32 \times 10^{13} e^{-20,340/RT}.$$

The values of K calculated from these expressions have been included in the last column in Table I.

E and A have not been calculated for the higher pressures, as the experimental accuracy was not sufficient.

It is clear that the change either in E or A as the pressure is increased, is not marked enough for a distinction to be made as to the relative importance of these two constants in determining the observed acceleration.

THE HYDROLYSIS OF SODIUM MONOCHLORACETATE BY SODIUM HYDROXIDE IN AQUEOUS SOLUTION

This reaction has been studied at atmospheric pressure by numerous workers, notably by Hedelius,* and by Schwab.† Good bimolecular constants were obtained which decreased slightly with decreasing concentrations. It has now been studied at temperatures between 40° and 80° C, and pressures up to 12,000 kg/cm² using 0.125 normal solutions.

The monochloroacetic acid was an "Analar" sample, used without further purification. The acid titre and the total chlorine content checked up to within 1% of the theoretical value.

Solutions of the acid and of sodium hydroxide were made up, the strength of the latter being double that of the former to allow for the formation of sodium monochloroacetate, and mixed. The course of the reaction was followed by taking samples, cooling to stop the reaction, and running into excess of standard sulphuric acid solution, and back titrating with caustic soda. In addition, the chloride ion concentration was determined by titration with silver nitrate using potassium chromate as an indicator.

* 'Z. phys. Chem.,' vol. 96, p. 343 (1920).

† Van't Hoff, "Chemical Dynamics," p. 129.

The constants were calculated from the ordinary bimolecular formula, small corrections being introduced to allow for the slight differences between the hydroxide and chloracetate concentrations. The actual values were taken as the mean of the two values found by the different methods of estimation.

TABLE II—THE HYDROLYSIS OF SODIUM MONOCHLORACETATE BY SODIUM HYDROXIDE IN AQUEOUS SOLUTION

Temperature ° C	Pressure kg/cm ²	Initial concentration	K' × 10 ³	K (obs.) × 10 ³	K (calc.) × 10 ³
40.1	1	0.125	0.419	0.422	0.425
50.05	1	0.125	1.31	1.32	1.34
55.0*	1	0.1	—	2.05	—
60.2	1	0.25	4.86	4.93	—
60.15	1	0.125	4.06	4.12	4.0
65.0*	1	0.1	—	6.08	—
70.15	1	0.125	10.8	11.0	10.9
80.25	1	0.125	26.8	27.5	28.2
80.0*	1	0.1	—	23.9	—
90.0*	1	0.1	—	61.8	—
40.0	2980	0.125	0.941	0.855	0.851
50.1	2980	0.125	2.86	2.63	2.63
60.1	2980	0.125	8.43	7.79	7.76
60.1	2980	0.25	10.03	9.27	—
70.05	2980	0.125	21.7	20.1	20.4
80.25	2980	0.125	55.6	51.9	52.5
60.1	5000	0.125	12.3	10.9	—
40.0	7600	0.125	2.6	2.18	2.19
60.1	7600	0.125	20.5	17.4	17.4
80.0	7600	0.125	126.0	107.0	107.0
60.1	8500	0.125	23.2	19.4	—
40.0	12,000	0.125	4.35	3.47	3.47
60.1	12,000	0.125	32.7	26.3	26.3
80.0	12,000	0.125	186.0	151.0	151.0

* Hedelius.

The results are given in Table II with those obtained by Hedelius, included for comparison. As can be seen from the two experiments in 0.25 normal solutions, a decrease in the initial concentrations causes a decrease in the constant, and taking this into account, the results are in excellent agreement with those of Hedelius.

Column 4 shows the constants (K') uncorrected for the compressibility and thermal expansion of the solution, and column 5 (K_{obs}) the corrected values, expressed as gram mol/litre/minute. It will be seen

that the velocity increases steadily with increase of pressure, the rate of reaction at 12,000 kg/cm² being about 6.5 times as great as that at 1 kg/cm².

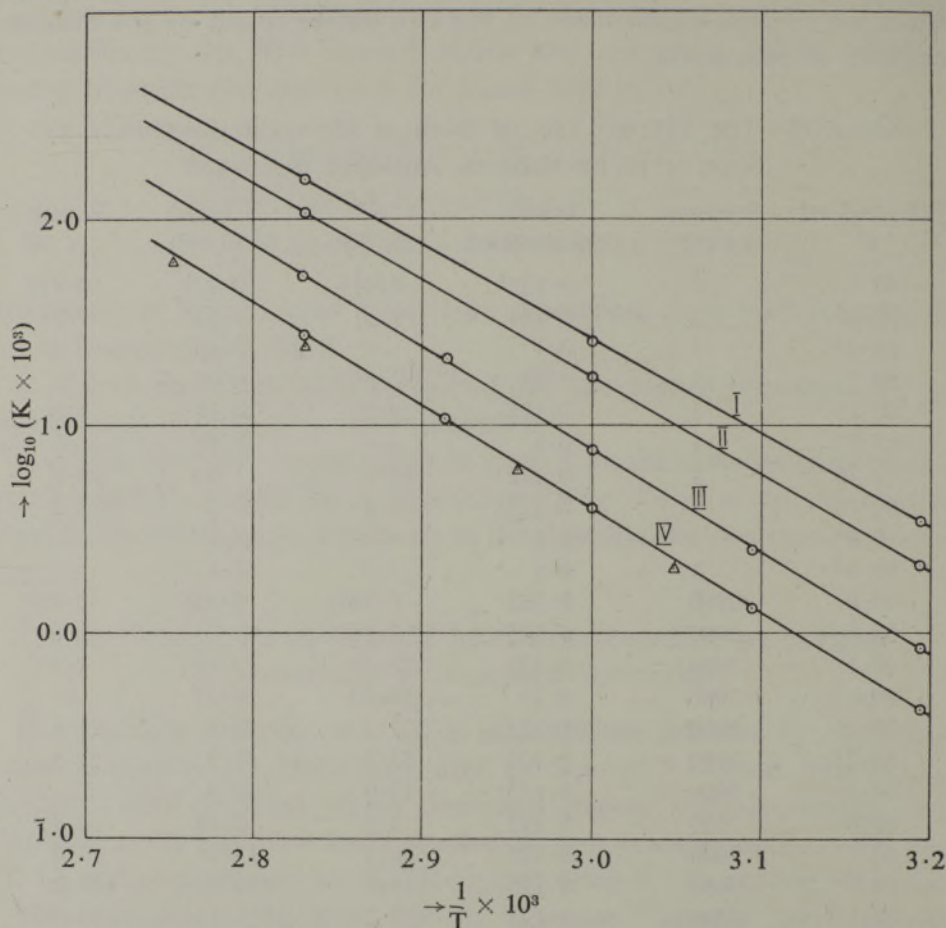


FIG. 1—I, 12,000 kg/cm²; II, 7600 kg/cm²; III, 3000 kg/cm²; IV, 1 kg/cm²; Δ Hedelius (0.1 N).

Fig. 1 shows $\log K$ plotted against $1/T$, and the calculated values of A and E , the constants of the Arrhenius equation, are given in the expressions below:

$$\text{for } 1 \text{ kg/cm}^2 \quad K = 3.5 \times 10^{12} e^{-22,730/RT}$$

$$\text{for } 2980 \text{ kg/cm}^2 \quad K = 4.07 \times 10^{12} e^{-22,440/RT}$$

$$\text{for } 7600 \text{ kg/cm}^2 \quad K = 1.78 \times 10^{12} e^{-21,330/RT}$$

$$\text{for } 12,000 \text{ kg/cm}^2 \quad K = 1.02 \times 10^{12} e^{-20,710/RT}.$$

The last column in Table II gives the values of the velocity constants calculated from these expressions.

There is a slight tendency for A to decrease with increasing pressure, so that the observed acceleration of the reaction must be due to the steady fall in E from 22,730 calories/gram mol at 1 kg/cm² to 20,710 at 12,000 kg/cm².

ESTERIFICATION OF ACETIC ANHYDRIDE WITH ETHYL ALCOHOL

This reaction has been studied in alcohol as solvent by Moelwyn-Hughes and Rolfe,* and in carbon tetrachloride and hexane by Hinshelwood and Moelwyn-Hughes.† The influence of the solvent on the reaction has also been studied by Menshutkin,‡ and by Soper and Williams.§

It has now been studied at 1, 1000, 2000, and 3000 kg/cm² between 15° and 45° C in ethyl alcohol as solvent, and between 20° and 80° C at 1 and 3000 kg/cm², and at 40° C up to 8500 kg/cm² in toluene. Individual runs to determine the pressure coefficient have also been made in acetone, hexane, and amyl ether at 1 and 3000 kg/cm².

Ethyl Alcohol—Absolute alcohol was dried over potassium carbonate and over calcium turnings. It was then carefully fractionated, the middle portion of constant refractive index ($n_{20} = 1.3618$; L.B.|| $n_{20}^D = 1.36175$) being collected and used.

Acetic Anhydride—A B.D.H. specimen was distilled through a long Dufton fractionating column, the first and last 25% being discarded. The middle fraction of constant refractive index, ($n_{20} = 1.3900$) was collected and used.

Toluene—A sample of A.R. sulphur free toluene was dried over phosphorus pentoxide and fractionated, the middle portion of constant refractive index ($n_{20} = 1.4962$) being collected and used.

Acetone—The acetone was dried, first over potassium carbonate and then calcium, and was then fractionated three times, the middle portion of constant refractive index ($n_{20} = 1.3590$; L.B. $n_{20}^D = 1.3593$) being collected and used.

Hexane—The hexane was dried over sodium wire and fractionated, the portion distilling between 68 and 69° C being collected. ($n_{20} = 1.3805$).¶

* 'J. Chem. Soc.', p. 241 (1932).

† *Ibid.*, p. 230 (1932).

‡ 'Z. phys. Chem.', vol. 1, p. 1611 (1887).

§ 'J. Chem. Soc.', p. 2297 (1931).

|| L.B., Landolt-Börnstein, "Tables," 5th ed.

¶ Gibson, Fawcett, and Perrin, 'Proc. Roy. Soc., A, vol. 150, p. 223 (1935).

Amyl Ether—A British Drug Houses specimen was dried over phosphorus pentoxide and twice fractionated. The 170–174° C portion was collected and used.

The solutions were made up separately by weight, and the anhydride concentration was checked by titration with baryta. In solvents other than ethyl alcohol, the anhydride and alcohol concentrations were adjusted to be exactly equal.

The reaction was followed by taking samples, chilling them, and pipetting 10 cc into 100 cc of cold distilled water. After standing for about 5 hours, during which time the anhydride was completely hydrolysed, the mixture was titrated against standard baryta solution, using phenolphthalein as indicator.

In ethyl alcohol the reaction is of the first order, and the percentage change in a given time is independent of the concentration. Thus no correction is necessary, in calculating the constants, for the thermal expansion or compressibility of the solution.

In other solvents the reaction is bimolecular, and the corrections become necessary. Unfortunately the compressibility of toluene has not been measured above 500 kg/cm², so that arbitrary values have had to be assumed. The compressibility has been assumed as 14% at 20° C, 15% at 40° C, 16% at 60° C, and 17% at 80° C, at 3000 kg/cm², and 18% and 21% at 40° C at 5000 kg/cm², and 8500 kg/cm² respectively. Since the compressibilities of different liquids are very similar, these assumed values are probably correct to 2 or 3%.

Ethyl Alcohol Solutions—The values of the constants for the reaction in ethyl alcohol as solvent are given in Table III with a few results from the work of Moelwyn-Hughes and Rolfe. The initial concentration of the acetic anhydride was 0.1 normal, and the constants are given in terms of gram mol/litre/minute. The reaction is accelerated some six or seven times at 3000 kg/cm².

Fig. 2 shows log K plotted against 1/T for the various pressures. It is clear that there is good agreement between the atmospheric pressure results and those of Moelwyn-Hughes and Rolfe.

The calculated values of E and A, the constants of the Arrhenius equation, are given below:

$$\text{for } 1 \text{ kg/cm}^2 \quad K = 385 \times 10^7 e^{-17,550/RT}$$

$$\text{for } 1000 \text{ kg/cm}^2 \quad K = 45.7 \times 10^7 e^{-15,900/RT}$$

$$\text{for } 2000 \text{ kg/cm}^2 \quad K = 39.26 \times 10^7 e^{-15,400/RT}$$

$$\text{for } 3000 \text{ kg/cm}^2 \quad K = 6.77 \times 10^7 e^{-14,000/RT}.$$

The values of K calculated from these expressions are included in the last column of Table III.

The considerable fall in the values of both E and A over this pressure range is very remarkable; its significance is discussed later.

Toluene Solutions—The values of the constants determined for the reaction in toluene solution are given in Table IV. The initial concentrations of both reagents were always 0.25 normal. K' represents the constant uncorrected for the thermal expansion and compressibility of the solvent, and K the corrected value.

TABLE III—ETHYL ALCOHOL AND ACETIC ANHYDRIDE IN ETHYL ALCOHOL SOLUTION

Temperature ° C	Pressure kg/cm ²	K (obs.) $\times 10^4$	K (calc.) $\times 10^4$
20	1	3.24	3.06
30	1	7.98	8.22
40	1	21.4	20.7
50.5*	1	48.9	51.3
60.0*	1	117.0	114.0
70.2*	1	260.0	254.0
20	1000	6.12	—
40	1000	35.1	—
20	2000	12.8	—
40	2000	70.0	—
15	3000	16.3	15.8
20	3000	23.9	23.9
30	3000	51.2	53.5
35	3000	78.5	77.3

* Moelwyn-Hughes and Rolfe.

The reaction is accelerated nearly four times at 3000 kg/cm², 7.4 times at 5000 kg/cm², and 45 times at 8500 kg/cm².

The calculated values of the constants A and E in the Arrhenius equation are given below:

$$\text{for } 1 \text{ kg/cm}^2 \quad K = 1.3 \times 10^8 e^{-15,250/RT}$$

$$\text{for } 3000 \text{ kg/cm}^2 \quad K = 8.5 \times 10^8 e^{-15,600/RT}$$

The values of K calculated from these expressions are included in the last column of Table IV.

The results indicate that this reaction is behaving similarly to the interaction of pyridine and ethyl iodide in acetone, where A increased rapidly with pressure, and E also increased slightly.

The reaction was not studied above 8500 kg/cm² for fear of the toluene freezing.

Other Solvents—The results for runs at various individual temperatures in amyl ether, acetone, toluene, and hexane are given in Table V.

It was very difficult to get reproducible results in acetone, but the values given are for acetone dried and distilled three times, and the same solutions

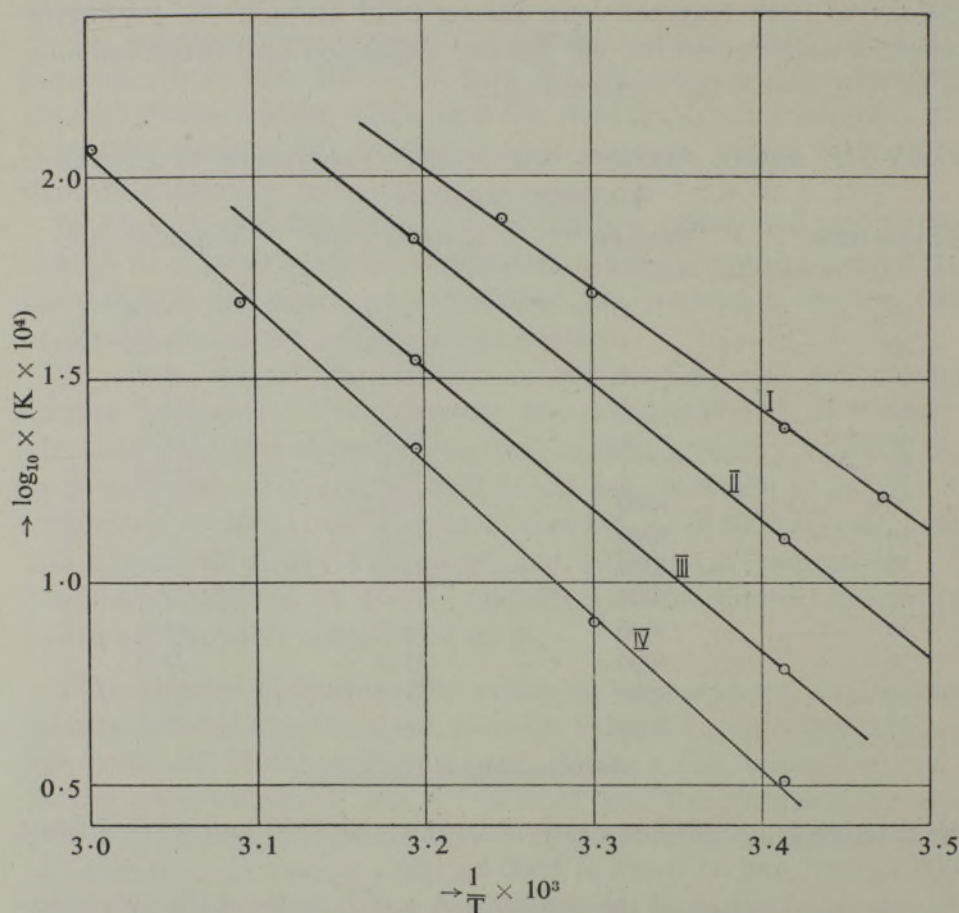


FIG. 2—I, 3000 kg/cm²; II, 2000 kg/cm²; III, 1000 kg/cm²; IV, 1 kg/cm².

were used for the 1 and 3000 kg/cm² experiments, so that the ratio of the constants should be trustworthy.

As the compressibilities of toluene and amyl ether are not known, no corrections have been introduced for any of the values in the table, and they are given in terms of the concentrations at 20° C and atmospheric pressure.

It is clear that the magnitude of the pressure effect varies from solvent to solvent, but that it is always of the same order.

TABLE IV—ETHYL ALCOHOL AND ACETIC ANHYDRIDE IN TOLUENE SOLUTION

Temperature ° C	Pressure kg/cm ²	K' (uncorrected) × 10 ²	K (obs.) × 10 ²	K (calc.) × 10 ²
20	1	0.054	0.054	0.055
40	1	0.2845	0.290	0.289
60	1	1.20	1.25	1.25
80	1	4.42	4.69	4.58
20	3000	0.2155	0.189	0.195
40	3000	1.24	1.10	1.07
60	3000	5.5	4.91	4.90
80	3000	19.8	17.8	18.2
40	5000	2.51	2.10	—
40	8500	16.1	13.0	—

TABLE V—THE EFFECT OF PRESSURE IN VARIOUS SOLVENTS

Solvent	Temperature ° C	K' (1 kg/cm ²)	K' (3000 kg/cm ²)	$\frac{K' (3000 \text{ kg/cm}^2)}{K' (1 \text{ kg/cm}^2)}$
Amyl ether.....	40	0.613×10^{-2}	1.88×10^{-2}	3.07
Acetone	80	0.39×10^{-2}	1.27×10^{-2}	3.26
Toluene	40	0.2845×10^{-2}	1.24×10^{-2}	4.35
Hexane	60	3.04×10^{-2}	17.0×10^{-2}	5.6

THE DECOMPOSITION OF PHENYL-BENZYL-METHYL-ALLYL AMMONIUM BROMIDE IN CHLOROFORM SOLUTION

This reaction has been studied at 25°, 35°, and 45° C at atmospheric pressure by von Halban,* who showed that the change in optical rotation observed by Pope and Harvey† was not due to racemization as had previously been supposed, but to decomposition of the salt with the formation of a tertiary base and an organic halide.

The reaction is unimolecular and was considered by von Halban to go to completion. The present work, however, has shown that it is reversible, and that even at atmospheric pressures at 25° C, it only goes to about 70% completion. At higher temperatures the decomposition goes further. It has been found that the equilibrium is shifted by pressure, and at 25° C and 3000 kg/cm² the decomposition only goes to about 30% completion.

A further complication arises from the change in the velocity constant with dilution, the constant in 0.025 normal solutions being almost double

* 'Ber. deuts. chem. Ges.,' vol. 41, p. 2417 (1908).

† 'J. Chem. Soc.,' vol. 79, p. 831 (1901).

that in 0.1 normal solutions. However, working with 0.1 normal solutions, the calculated unimolecular velocity constants remain steady throughout a given run, at any rate up to about 60–70% conversion, although with 0.025 normal solutions, a definite drift in the values is apparent as the run proceeds.

The phenyl-benzyl-methyl-allyl ammonium bromide was prepared from methyl-benzyl-aniline and allyl bromide.

Methyl Benzyl Aniline—A B.D.H. specimen was purified by twice fractionating *in vacuo*. The fraction collected was about 60% of the whole, and came over at 125° C at about 1 mm pressure.

Allyl Bromide—A B.D.H. specimen was twice distilled through a fractionating column, the middle portion, about 60% of the whole, being collected. (B.P. 69–71° C.)

In preparing the ammonium salt, equimolecular portions of the methyl benzyl aniline and allyl bromide were dissolved in alcohol and left to stand overnight at room temperature. The solution was seeded, and the resulting crop of crystals filtered off. The product was then recrystallized by dissolving in chloroform and precipitating by addition of acetone. Fine pure white crystals were obtained which melted sharply at 144° C. Repeated recrystallization of a small sample caused no change in the melting point. It may be noted that the melting point of the salt is given in Beilstein as 161–163° C. Nevertheless, the extreme sharpness of the melting point, and the fact that repeated recrystallization caused no change, showed that the product was pure, and the excellent agreement obtained with the constants measured by von Halban, shows that the salt was identical with that used by him.

Chloroform—B.D.H. “Analar” chloroform was dried over calcium chloride and fractionated through a long Dufton column, the portion distilling at 60.5° C being collected.

(Refractive index $n_{20} = 1.4459$; L.B. $n_{20}^D = 1.4472$.)

The method of analysis, was the same as that used by von Halban, namely the estimation of the ionizable halogen by taking samples from time to time and running them into a known excess of silver nitrate solution, and back titrating with thiocyanate using ferric alum as an indicator.

A special formula has been used in calculating the unimolecular constants. If a is the initial concentration of the salt and x the concentration of the part which has reacted after t minutes, then

$$\frac{dx}{dt} = K(a - x) - K'x^2,$$

where K and K' are the velocity constants of the unimolecular decomposition, and the reverse bimolecular association respectively. On integration this gives:

$$K = \frac{1}{(4a\alpha + 1)^{\frac{1}{2}} (t_1 - t_0)} \log_e \frac{2\alpha x_1 + 1 + (4a\alpha + 1)^{\frac{1}{2}}}{2\alpha x_1 + 1 - (4a\alpha + 1)^{\frac{1}{2}}} \\ \times \frac{2\alpha x_0 + 1 - (4a\alpha + 1)^{\frac{1}{2}}}{2\alpha x_0 + 1 + (4a\alpha + 1)^{\frac{1}{2}}},$$

where α , the equilibrium constant, equals K'/K , and x_1 and x_0 are the concentrations of the decomposed portions after t_1 and t_0 minutes respectively.

The compressibility of chloroform is not known at 3000 kg/cm² but has been assumed as 13% at all the temperatures considered. The constants have been corrected on this assumption, which is probably not far out, and in any case, the correction affects the values of the unimolecular constants K very slightly.

In each case the values of α were determined from the end point of the reaction; they are not very reliable, partly because the equilibrium frequently lay very much on one side, and partly because a certain amount of discoloration and decomposition occurred during the long time necessary for the end point to be reached. Large errors in α , however, cause only small corresponding errors in K , particularly as points during the runs have not been taken too close to the end point.

The results are given in Table VI, which includes the values of α , K , and K' , K' being the product of α and K . The solutions were 0.1 normal and the constants are expressed as gram mol/litre/minute.

The interesting result emerges, that the unimolecular decomposition is definitely retarded by pressure. The constants at 3000 kg/cm² are all about 1.5 times less than the corresponding constants at 1 kg/cm².

The effect of dilution is shown in Table VII which gives the constants at 45° C in 0.0975, 0.0537, 0.034, and 0.0255 normal solutions. The original intention was to carry out runs at two concentrations at each temperature, so as to have a check on the values of α and K , but this was not feasible, owing to the large dilution effect.

Although the actual values of K' are not very reliable, the mean of the ratios of the values at 3000 kg/cm² to the corresponding values at 1 kg/cm² is 5.6, a figure which corresponds very well with the acceleration observed at this pressure in other bimolecular reactions of the "slow" class.

696 E. G. Williams, M. W. Perrin, and R. O. Gibson

The calculated values of A and E, the constants of the Arrhenius equation, are given below:

$$\text{for } 1 \text{ kg/cm}^2 \quad K = 18.6 \times 10^{17} e^{-29,660/RT}$$

$$\text{for } 3000 \text{ kg/cm}^2 \quad K = 6.0 \times 10^{17} e^{-29,200/RT}.$$

The values of K calculated from these expressions are included in Table VI.

TABLE VI—DECOMPOSITION OF PHENYL-BENZYL-METHYL-ALLYL AMMONIUM BROMIDE IN CHLOROFORM SOLUTION

Temperature °C	Pressure kg/cm ²	Initial concn.	α	K (obs.) $\times 10^4$	K (calc.) $\times 10^4$	K' $\times 10^2$
25.0	1	0.0975	7.97	3.23	3.16	0.258
29.95	1	0.0975	5.1	7.4	7.1	0.377
34.95	1	0.0975	2.21	15.8	15.85	0.350
39.9	1	0.0975	1.44	34.3	34.7	0.493
44.9	1	0.0975	0.64	74.5	73.0	0.478
25.0	2980	0.0975	75.5	2.16	2.24	1.63
29.95	2980	0.0975	34.0	5.1	4.9	1.74
34.95	2980	0.0975	16.8	10.7	10.9	1.80
40.0	2980	0.0975	10.6	22.9	2.34	2.43
44.9	2980	0.0975	7.37	47.6	48.9	3.51
25.0*	1	—	—	3.13	—	—
35.0*	1	—	—	15.55	—	—
45.0*	1	—	—	76.0	—	—
25.0	1	0.0249	—	5.95	—	—
34.9	1	0.0265	—	26.6	—	—
45.0	1	0.0255	—	118.0	—	—
25.0	2980	0.0247	39.7	3.95	—	1.57
34.9	2980	0.0250	—	18.0	—	—
45.0	2980	0.0226	—	91.3	—	—

* von Halban.

TABLE VII—THE EFFECT OF DILUTION AT 45° C AND 1 ATMOSPHERE

Initial concentration	K	Initial concentration	K
0.0975	74.5×10^{-4}	0.0340	106×10^{-4}
0.0537	87.0×10^{-4}	0.0255	118×10^{-4}

DISCUSSION

We may now review the results as a whole. Fig. 3 shows the effect of pressure on the velocity constants of the various reactions. For purposes

of comparison K_p/K_0 has been plotted against P , where K_p and K_0 are the constants at P kg/cm² and 1 kg/cm² respectively.

It is clear that the reactions fall into three main classes:—

(1) “Normal” Reactions—That is, bimolecular reactions involving ions, where pressure has an accelerating influence, but where this effect is not large, and does not increase particularly rapidly with rising pressure. This is the behaviour shown by the interaction of sodium ethoxide

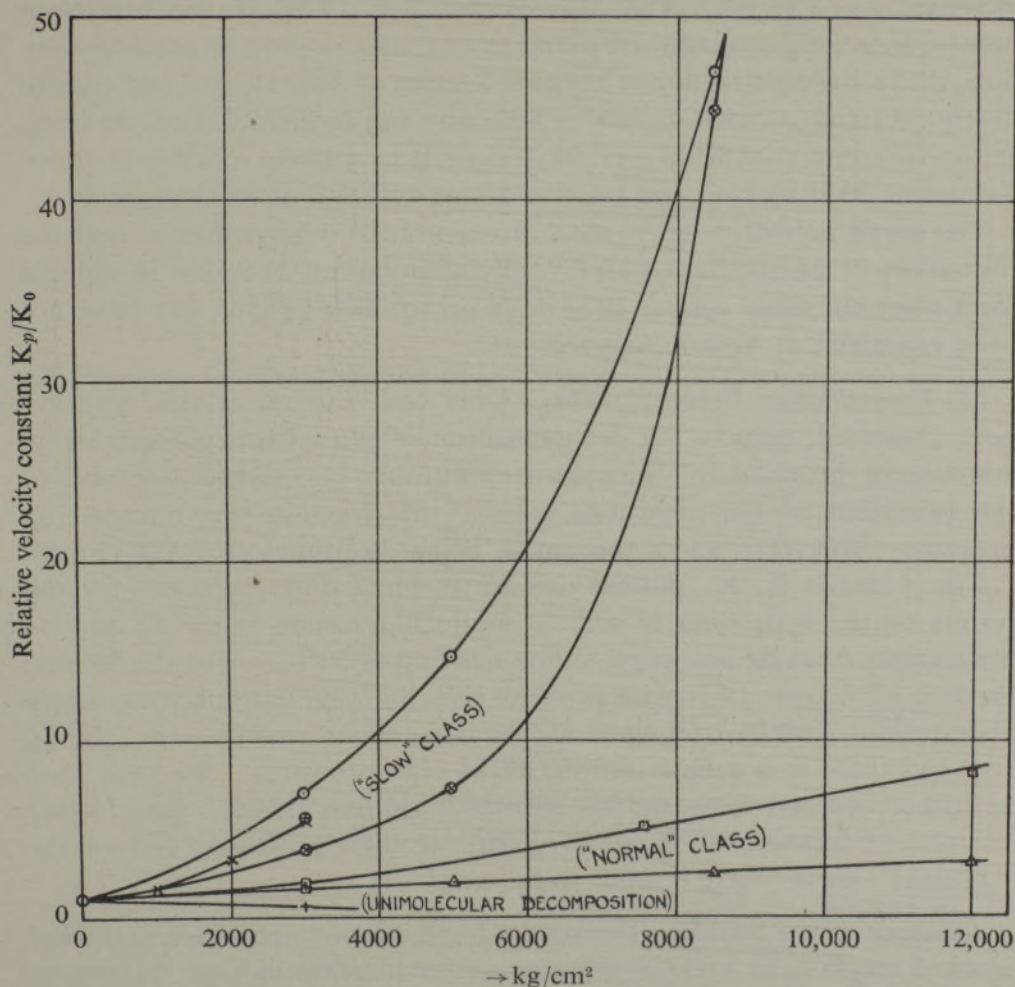


FIG. 3—○ Pyridine and ethyl iodide in acetone, at 40° C; ⊗ acetic anhydride and ethyl alcohol in toluene, at 40° C; × acetic anhydride and ethyl alcohol in alcohol, 40° C; ⊕ formation of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform, 30° C; □ hydrolysis of sodium monochlorate by aqueous caustic soda, 40° C; △ sodium ethoxide and ethyl iodide in ethyl alcohol solution, 30° C; + decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform, 30° C.

and ethyl iodide in ethyl alcohol solution, where the acceleration is 1.6 times at 3000 kg/cm², and rises to about 3 times at 12,000 kg/cm²; also by the hydrolysis of sodium monochloracetate by aqueous caustic soda, where the acceleration is about 2 times at 3000 kg/cm², and rises to about 8 times at 12,000 kg/cm².

(2) "*Slow*" *Reactions*—That is, bimolecular reactions between neutral molecules, where pressure has a greater accelerating influence, which also increases more rapidly with rise of pressure. This is the behaviour observed in the interaction of pyridine and ethyl iodide in acetone solution, where the acceleration is about 7.2 times at 3000 kg/cm² and rises to nearly 50 times at 8500 kg/cm². Similarly the acceleration of the interaction of acetic anhydride and ethyl alcohol in toluene solution is about 4 times at 3000 kg/cm², and rises to about 45 times at 8500 kg/cm².

The acetic anhydride-ethyl alcohol reaction in other solvents, and the formation of phenyl-benzyl-methyl-allyl-ammonium bromide in chloroform solution, show similar behaviour up to 3000 kg/cm², but have not been examined at higher pressures.

(3) *Unimolecular Decompositions*—Only one reaction of this type has been examined, namely the decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform solution. In marked contrast to the behaviour of the other two classes, this reaction was retarded by pressure. The retardation was small, being 1.5 times at 3000 kg/cm².

Fig. 4 shows K_p/K_0 plotted against P , on a different scale, for the results on the hydrolysis of sodium monochloracetate at 60° C, and on the sodium ethoxide and ethyl iodide reaction at 30° C. For the former, the rate of increase of K with pressure rises initially, but falls away again above about 7000 kg/cm², while for the latter there is no detectable initial rise, but there is a definite falling off at high pressures. We thus have a further contrast between the behaviour of the "slow" class, where the rate of increase of K rises rapidly at high pressures, and of the "normal" class, where it tends to fall away.

Influence of the Solvent—The results for the acetic anhydride and ethyl alcohol reaction in various solvents at 1 and 3000 kg/cm², have been given in Table V. The pressure effect is greatest in hexane, rather less in toluene, and least in amyl ether and acetone. Amyl ether was selected on account of the very rapid increase of its viscosity with pressure,* and the small acceleration in this solvent indicates that the viscosity plays very little part. There is no readily apparent property of the various

* Bridgman, "The Physics of High Pressure," Bell, p. 341 (1931).

solvents, which can be coordinated with the magnitude of the pressure effects observed in them.

This same reaction in excess alcohol as solvent is of interest from the point of view of the theory of solvent-solute collisions. It is usually considered that the number of collisions between solute and solvent molecules is proportional to the viscosity of the solvent.* The viscosity of ethyl alcohol under pressure has been measured by Bridgman,† and increases roughly 1.6 times at 1000 kg/cm², and 3.2 times at 3000 kg/cm².

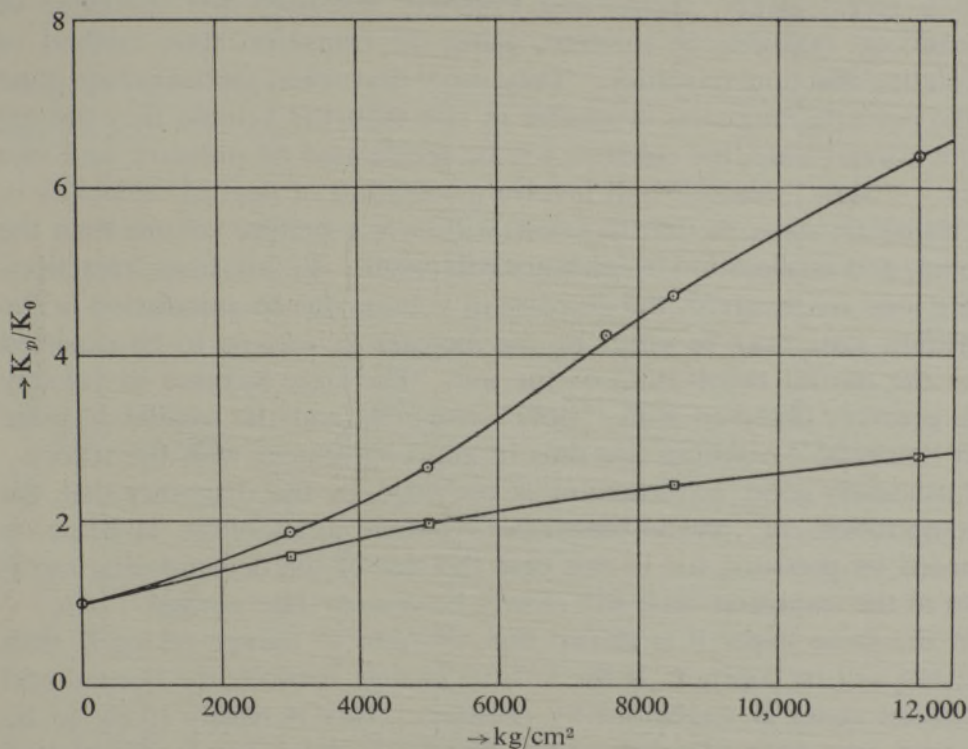


FIG. 4—○ Hydrolysis of monochloracetate by aqueous caustic soda, 60° C; □ interaction of sodium ethoxide and ethyl iodide in ethyl alcohol, 30° C.

We should therefore expect the collision number to increase in the same proportion. It is found, however, that although the reaction is accelerated by pressure, this acceleration is due to a large decrease in E , while the A term of the Arrhenius equation falls off rapidly.

Referring to the figures given on p. 690 it can be seen that the A term at 3000 kg/cm² is 57 times less than at 1 kg/cm². The changes in E are so large as to make it difficult to believe that they represent true changes in

* Cf. Moelwyn-Hughes, "Kinetics of Reaction in Solution," p. 18, Oxford, 1933.

† Bridgman, "The Physics of High Pressure," Bell, p. 341 (1935).

the critical activation energy. It seems probable that there is some other independent factor operating, which is a function of the temperature. This cannot be the viscosity, since over this range of pressure, the viscosity temperature coefficient of ethyl alcohol is almost constant; the matter may however be connected with changes in the nature of the solvent due to association.

THE NATURE OF THE PRESSURE EFFECT

In a recent paper, Evans and Polanyi* discussed the influence of pressure on reactions in solution, using the transition state method of calculating reaction velocities. They show that when the transition state of the reacting molecules is smaller in size than the volume they occupy in the normal state, the reaction will be accelerated by pressure, and vice versa. "Slow" reactions all involve association of neutral molecules in the transition state, so that this state will have a smaller volume than the normal, and acceleration by pressure will result. In "normal" reactions where ions are involved, the decrease in volume due to association in the transition state may be offset by the increase in volume to be expected from the partial desolvation of the ion. The large increase in velocity with pressure observed with "slow" reactions and the smaller increase with "normal" reactions are thus in good agreement with the theory.

Particularly good confirmation is provided by the discovery that the decomposition of phenyl-benzyl-methyl-allyl ammonium bromide is retarded by pressure, for in this case the size of the decomposing molecules in the transition state will clearly be greater than normal.

In the same paper it is shown that the rate of change of $\log K$ with pressure will be constant, if the volume change between the normal and transition states is unaffected by pressure. This is hardly likely to be the case over wide pressure ranges, but fig. 5 shows $\log K_p/K_0$ plotted against P for the two "slow" reactions. It will be seen that for the ethyl iodide pyridine reaction, the rate of increase of $\log K$ falls off as the pressure increases, but that for the acetic anhydride and ethyl alcohol reaction it is approximately constant.

The equation for the velocity constant of a reaction may be written in the form $K = P \cdot Z \cdot e^{-E/RT}$, where Z is the number of collisions between the reacting molecules, E the energy of activation, and P the probability that a collision with the requisite energy will lead to reaction.

The A term of the Arrhenius equation is thus equal to PZ . For bi-molecular reactions in solution, there is no reason to suppose that Z will

* 'Trans. Faraday Soc.,' vol. 31, p. 875 (1935).

vary much with increase of pressure, so that changes in A will be mainly due to changes in the factor P .

For the two "normal" reactions, where P is of the order of unity, the A term fluctuates somewhat, though if anything it appears to fall off with rising pressure. The activation energy E appears to decrease as the pressure increases. Within the limits of experimental accuracy, the observed

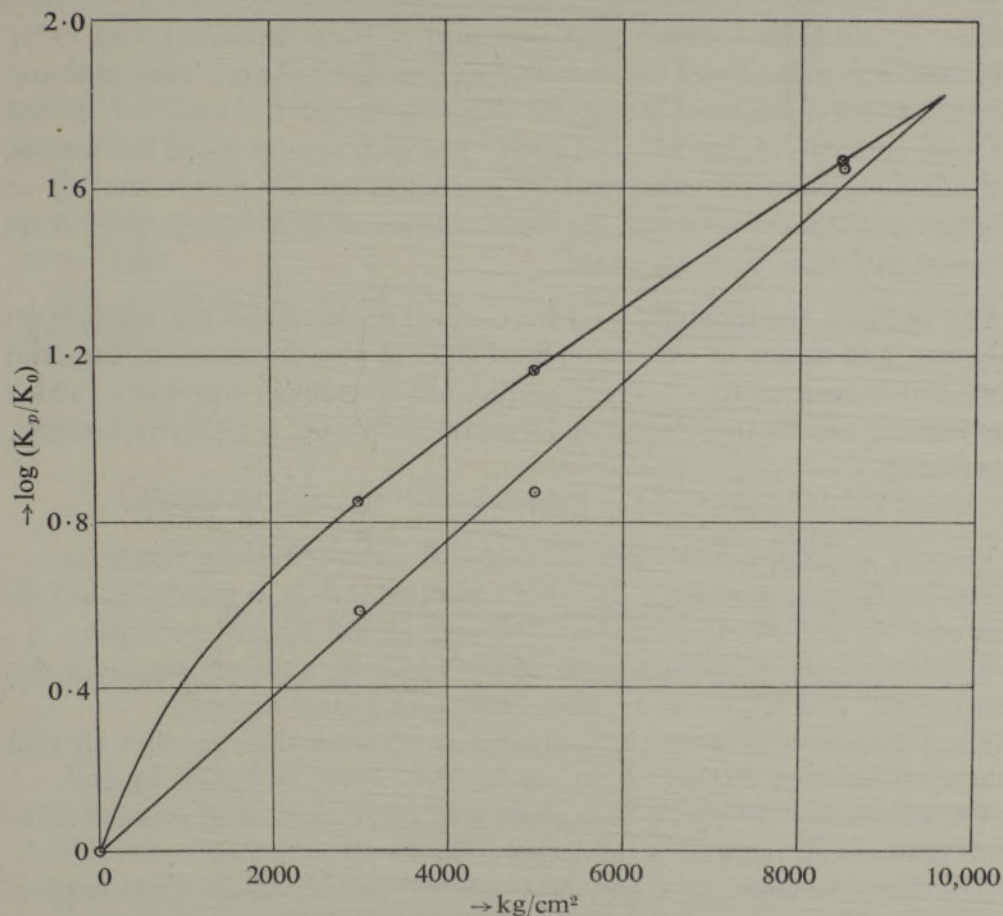


FIG. 5—○ Acetic anhydride and ethyl alcohol in toluene solution, 40° C; ⊗ pyridine and ethyl iodide in acetone solution, 40° C.

acceleration of the reactions can be ascribed to the changes in E and it appears a reasonable assumption that the increase in velocity is due to the fact that some or all of the energy of compression is available as activation energy.

For the "slow" reactions, in inert solvents, the "temperature independent" term and the activation energy both rise with pressure. The increase in A , which more than counteracts the increase in E , is presumably

due to a large increase of P , which is of the order of 10^{-4} – 10^{-8} , with pressure. Where the "slow" reaction, on the other hand, takes place in excess of one of the reactants as solvent both A and E decrease with increasing pressure although the net effect of pressure on the rate is of the same order as in inert solvents. In this case some complicating factor due to the effect of pressure on the collision rate may be introduced.

It may be noted that in all the reactions so far examined, of both classes, A and E have either both increased or both decreased with rising pressure, but have never moved in opposite directions. This indicates some connexion between P and E . The nature of the factor P , is not yet fully understood, but Hinshelwood* has recently discussed the matter, and concludes that its value will be increased by any factor tending to lengthen the duration of the requisite collisions, and it is possible that pressure produces such an effect.

The authors are indebted to Mr. C. N. Hinshelwood for his helpful criticism, and desire to express their thanks to the Directors of Imperial Chemical Industries Limited, for permission to publish this work, which was carried out in the Research Department of I.C.I. (Alkali) Limited, Northwich.

SUMMARY

Velocity constants have been measured for the following reactions:

The interaction of sodium ethoxide and ethyl iodide in alcohol solution, between 15° and 30° C at 5000, 8500, and 12,000 kg/cm² pressure.

The hydrolysis of sodium monochloracetate by aqueous caustic soda, between 40° and 80° C, at 1, 3000, 7600, and 12,000 kg/cm².

The interaction of acetic anhydride and ethyl alcohol in ethyl alcohol solutions, between 15° and 40° C at 1, 1000, 2000, and 3000 kg/cm².

The interaction of acetic anhydride and ethyl alcohol in toluene solutions between 20° and 80° C at 1 and 3000 kg/cm².

The same reaction at 1 and 3000 kg/cm² at individual temperatures, in acetone, hexane, and amyl ether solutions.

The decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform solution between 25° and 45° C at 1 and 3000 kg/cm².

The constants A and E of the Arrhenius equation have been calculated wherever possible.

The reactions fall into three main classes:—

(a) "Normal" Reactions—Where pressure has a small accelerating influence which falls off at high pressures, the increase in velocity being

* 'J. Chem. Soc.,' p. 1111 (1935).

of the order of 5 times at 12,000 kg/cm². The acceleration in this class appears to be due mainly to a decrease in the activation energy.

(b) "*Slow*" Reactions—Where pressure has a much greater accelerating influence, which increases with increasing pressure, the increase in velocity being of the order of 10 times at 5000 kg/cm², and 45 times at 8500 kg/cm². In this class the constants A and E of the Arrhenius equation both increase with increasing pressure.

(c) *Unimolecular Decompositions*—The decomposition of phenyl-benzyl-methyl-allyl ammonium bromide in chloroform solution is retarded 1.5 times at 3000 kg/cm².

The magnitude of the pressure effect on the ethyl alcohol and acetic anhydride reaction varies with change of solvent, but is always of the same order.

The results are in good agreement with the predictions given by the transition state method of calculating reaction velocities.

A Comparison of the Absorption Spectra of Some Typical Symmetrical Cyanine Dyes

By NELLIE I. FISHER and FRANCES M. HAMER

(Communicated by Sir William Pope, F.R.S.—Received December 17, 1935)

INTRODUCTION

Compounds of the cyanine type show a wide variation in colour, whilst possessing comparatively simple chemical structures. They are, therefore, particularly suitable for a study of the relationship between colour and constitution. Such a study, for certain fairly simple series of cyanine dyes, free from substituents, forms the subject of the present paper.

The cyanines are characterized by possessing two heterocyclic nuclei containing nitrogen. One of our objects was to find how the colour varies according to the nature of the nuclei, but we restricted the investigation to those series in which the two nuclei are identical.

According to static formulae for compounds of the cyanine type, the nitrogen atom of one heterocyclic nucleus is tertiary, and that of the other is quaternary; the nitrogen atoms are joined by a chain of conjugated linkages, so that the number of carbon atoms in the chain is