46. *The Functional Relation between the Constants of the Arrhenius Equation. Solvent Effects in a Diels–Alder Addition.*

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The dependence upon the polarity of the solvent of the term PZ in the reaction velocity equation $k = PZe^{-E/RT}$ in an example of the Diels–Alder addition is compared with that previously studied for quaternary ammonium salt formation. Since in highly polar solvents an increase in PZ at constant activation energy is still found, though of considerably diminished magnitude, the effect cannot be wholly explained as an increase in P due to the stabilisation of a polar product, but may be partly due to this and to an actual change in the collision frequency, Z.

In a previous communication (J., 1937, 1573) the rate of formation of methylpyridinium iodide in various solvents was studied, the results being analysed in terms of the equation $k = PZe^{-E/RT}$. The total variation of log PZ could be accounted for by assuming a general correlation between log PZ and E, together with a tendency for log PZ to increase in the more polar solvents. Two alternative kinds of explanation were indicated. On the one hand, individual molecules of the solvent might increase P by stabilising molecules of the polar product which would otherwise revert into their constituents (cf. Hinshelwood, *Trans. Faraday Soc.*, 1936, **32**, 970 ; 1938, **34**, 138). On the other hand, the conditions in a polar solvent might be such as to produce an actual increase in the frequency of the encounters between the reactant moelcules, *i.e.*, to increase Z itself.

The present experiments were designed in the hope of estimating the relative importance of these two factors. If the influence of the polar solvents is due to a stabilisation of a polar product then it should only be observed in reactions where such a product is formed, whereas if it depends upon changes in Z then it should be equally in evidence when the product is non-polar. The reaction chosen for investigation was the condensation of *cyclo*pentadiene with benzoquinone, which gives a product of very low polarity (Wassermann, J., 1935, 828). It was studied in carbon tetrachloride, benzene, nitrobenzene, and benzonitrile.

*cyclo*Pentadiene was prepared by the destructive distillation of di*cyclo*pentadiene in the presence of iron wire in an apparatus fitted with a Dufton column wound with nickel wire. The diene distilled over at 40°, and was collected in a small weighed tube of thin glass, which was sealed, weighed, and then broken under the surface of a known volume of solvent. Solutions were always used within a few hours, and usually within a few minutes, of preparation. In some experiments the diene was distilled in a current of dry oxygen-free nitrogen, and in others in air, but no difference in the reaction rate was observed.

Benzoquinone was recrystallised from hexane. Specially purified medicinal carbon tetrachloride was used : benzene, nitrobenzene, and benzonitrile were fractionated in an all-glass apparatus. The benzene had been dried over sodium, and the nitrobenzene over calcium chloride.

The rate of reaction was followed by the colorimetric method described by Wassermann. The decrease in colour as the quinone reacted was measured with a Zeiss Pulfrich Stufen-photometer using filter S47. Equal volumes of solutions of the reactants, N/100 before mixing, were preheated, mixed, and placed in a 15-cm. all-glass polarimeter tube with a ground-glass

stopper. The tube was held in a small brass tank with glass windows, and water was circulated from an electrically controlled thermostat. A thermometer in the tank was found to vary by less than 0·1°. It was compared with an N.P.L. standard.

The logarithms of the readings on the scale of the photometer were found to be directly proportional to the concentration of the quinone. Readings were taken at frequent intervals during a run, and their logarithms plotted against time. From the best smooth curve drawn through these points, bimolecular constants were calculated. The reaction was found to follow the bimolecular law and the Arrhenius equation in each solvent. The rate was measured in benzene at five temperatures, and in other solvents at six, in the range 10—50°. All constants were corrected for solvent expansion. The following table shows typical experiments in benzene and in nitrobenzene.

Benzene; 27·2°.			Nitrobenzene; 40·8°.		
Mins.	% changed.	k.	Mins.	% changed.	k.
32	10	0·0118	7	10	0·0523
50	15	0·0120	10·5	15	0·0560
69	20	0·0121	14	20	0·0596
91	25	0·0122	19·2	25	0·0576
114	30	0·0125	24	30	0·0596
145	35	0·0123	29	35	0·0610
179	40	0·0124	35	40	0·0630
228	45	0·0119	135	70	0·0576
295	50	0·0113			

Mean 0·0120 (l./g.-mol.)/sec.,   Mean 0·0583 (l./g.-mol.)/sec.,
both uncorrected for solvent expansion.

Values of E and log PZ were calculated by the method of least squares. The " probable error " in E was calculated and in each case was of the order 250 calories. The values obtained were as follows :

Solvent.	E.	log PZ.	Solvent.	E.	log PZ.
Carbon tetrachloride	8,400	4·03	Nitrobenzene	8,800	4·99
Benzene	11,500	6·31	Benzonitrile	8,000	4·50

The values for carbon tetrachloride and benzene agree with those obtained by Wassermann (J., 1936, 1028; *Ber.*, 1933, **66**, 1392), but the values for E and log PZ in nitrobenzene are somewhat lower than his values (*Trans. Faraday Soc.*, in the press).

In the figure our values for log PZ are plotted against $E^{-\frac{1}{2}}$ (compare J., 1937, 538), together with values for hexane and for ethyl alcohol taken from Wassermann. The points for the three polar solvents lie on one straight line, and those for the three non-polar solvents upon a parallel line. For the same activation energy, log PZ is approximately 0·7 greater in the polar solvents. Thus in this respect there is a qualitative similarity between this reaction and the formation of quaternary ammonium salts, *i.e.*, there is a tendency for E to increase in polar solvents, superimposed upon a general correlation between log PZ and E.

It is interesting to compare the magnitudes of the effect in the three clear cases where it has been found to exist. For a given activation energy the formation of methylpyridinium iodide occurs about 30 times as fast in the group of highly polar solvents as in the non-polar ones : the formation of allylpyridinium bromide approximately 15 times as fast (Hawkins, J., 1922, **121**, 1170; cf. J., 1937, 544, Fig. 3), and the addition of benzoquinone to *cyclo*pentadiene approximately 5 times. Thus, although the effect appears in
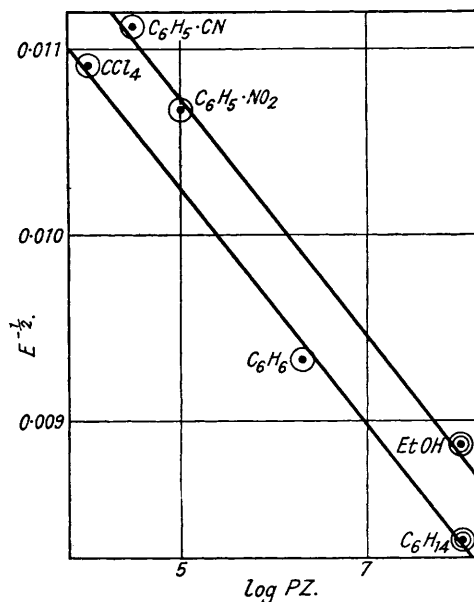
the Diels–Alder reaction, it is smaller. These results do not decide definitely in favour of either of the mechanisms discussed above. The fact that the influence of polarity appears at all in the Diels–Alder reaction shows that the stabilisation of a polar product cannot be the whole story. Some part of the effect may be due to an actual increase in the collision frequency in the polar solvents. But we may still assume with some probability that the large magnitude of the polar influence in quaternary ammonium salt formation is connected with the stabilisation process.

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