

**329.** *The Functional Relation between the Constants of the Arrhenius Equation. Solvent Effects in the Formation of Quaternary Ammonium Salts.*

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Reaction velocity can be expressed in the form  $PZe^{-E/RT}$ , where  $E$  is activation energy,  $Z$  the collision number, and  $P$  a probability factor, the nature of which forms the subject of various recent investigations. In a previous paper correlations between  $E$  and  $\log PZ$  for various series of reactions were studied experimentally and theoretically. In the present paper the formation of methylpyridinium iodide is studied in binary mixtures of various solvents. The variations of  $PZ$  with solvent composition are of diverse and complicated types, in spite of which it is found that they can be analysed into a general correlation between  $\log PZ$  and  $E$  together with a uniform tendency for  $PZ$  to increase with the polarity of the solvent.

In a previous communication (this vol., p. 538) the correlation existing for many reactions between the quantities  $E$  and  $\log PZ$  of the Arrhenius equation was discussed. A simple relation was found to hold for change of solvent in many cases. In the formation of quaternary ammonium salts, two effects appeared to be superimposed, namely, the normal correlation between  $E$  and  $\log PZ$  through a series of solvents of approximately the same polarity, and a general tendency for  $P$  to increase in the more polar solvents.

The object of the experiments to be described was to confirm and extend these conclusions. The plan was to study the variations of  $E$  and of  $\log PZ$  for the formation of methylpyridinium iodide in binary solvent mixtures of different types, including polar-polar and polar-non-polar systems. The activation energy varies with solvent composition according to curves of diverse and occasionally complicated form (Fig. 1). The form of the curves for  $\log PZ$  against composition tends to follow that of the corresponding activation energy curve, showing that the correlation between  $\log PZ$  and  $E$  is at least one important factor (see continuous lines in Figs. 2—6). By assuming the form of correlation found to hold in the previous paper for many reactions, all the values of  $\log PZ$  can be reduced to correspond to a standard activation energy. If no other factor were involved, the reduced values would all be the same. Actually they vary, but the residual variation is of the same simple form in each case, being a steady and regular increase with increasing solvent polarity. The fact that widely divergent types of behaviour can all be reduced in this way to a single simple form of variation justifies the suggested analysis of the effect into two factors. It is therefore concluded that the functional relation between  $E$  and  $\log PZ$  previously advanced applies generally to solvent changes in the formation of quaternary ammonium salts, but that, in addition to the changes of  $\log PZ$  produced in this way, there is also a variation which is independent of the energy of activation, but dependent on the polarity of the solvent.

*Experimental Results.*—The general procedure was that described in the previous paper. The various solvents were fractionated in an all-glass apparatus after being dried with

FIG. 1.

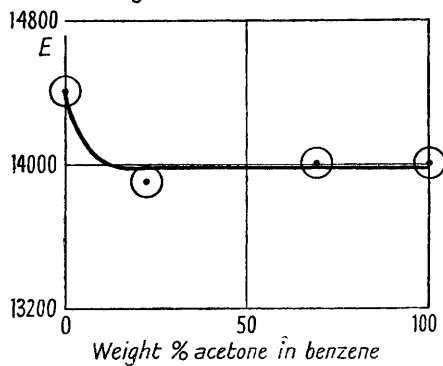
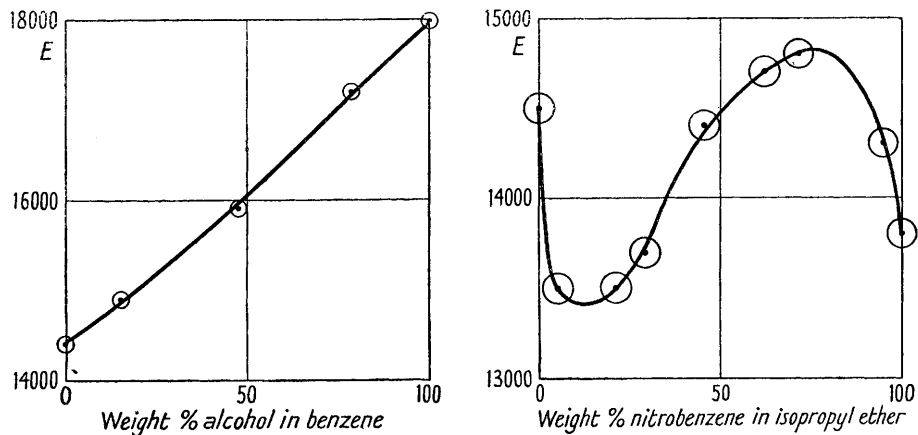


FIG. 2.

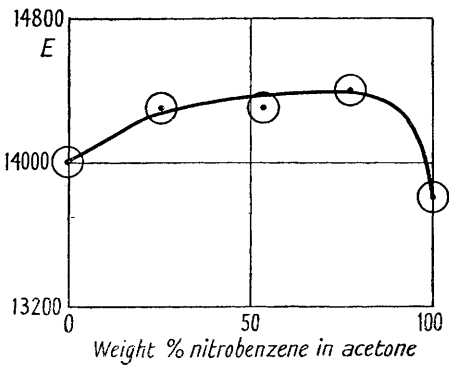
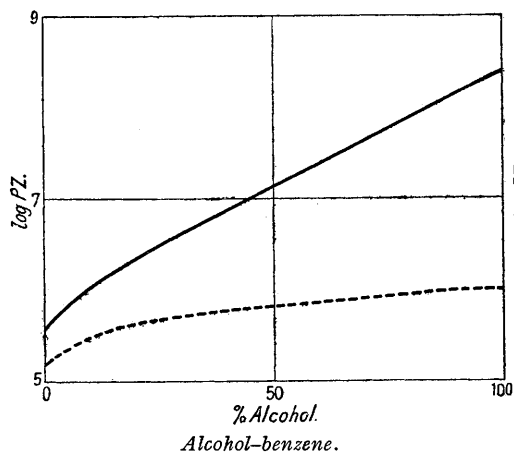
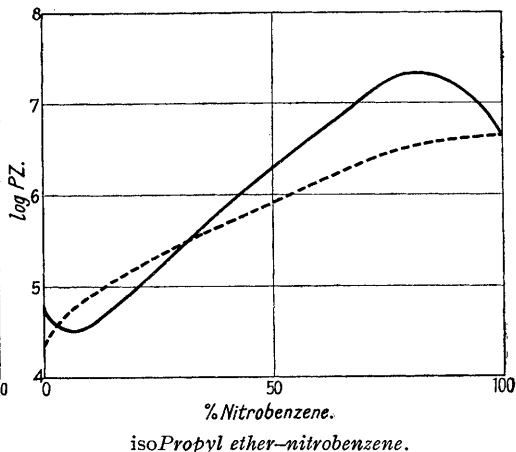


FIG. 3.



Alcohol-benzene.

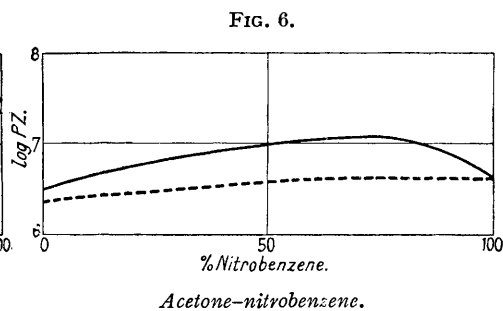
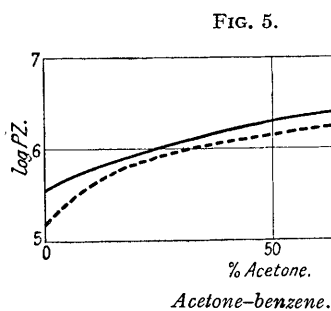
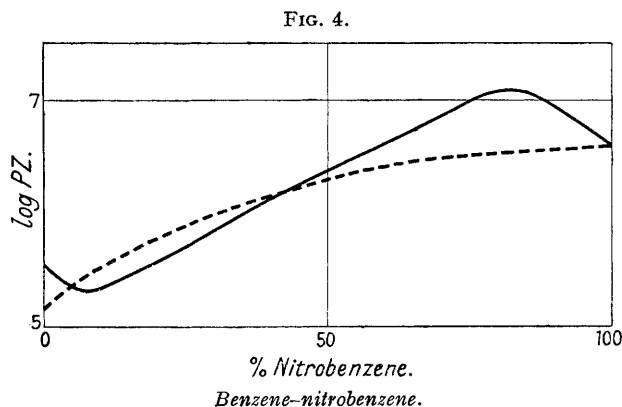


isoPropyl ether-nitrobenzene.

appropriate agents (sodium for benzene and *isopropyl ether*, lime for alcohol, and calcium chloride for nitrobenzene).

In calculating velocity constants, correction was made for thermal expansion of solvents. Activation energies were determined from measurements at four temperatures in the range

either 25—80° or 40—100°. In general, we estimate their accuracy to be of the order  $\pm 150$  cal.



The following tables give the values of  $E$  and of  $\log PZ$  for the various systems.

Alcohol-Benzene.			Benzene-Nitrobenzene.			isoPropyl ether-Nitrobenzene.		
EtOH, wt. %.	$E$ .	$\log PZ$ .	Ph·NO <sub>2</sub> , wt. %.	$E$ .	$\log PZ$ .	Ph·NO <sub>2</sub> , wt. %.	$E$ .	$\log PZ$ .
0	14,400	5.55	0	14,400	5.55	0	14,500	4.77
15.5	14,900	6.28	8.35	13,700	5.32	5.2	13,500	4.53
47.5	15,900	6.99	31.2	13,600	5.88	21.6	13,500	5.03
78.3	17,200	7.86	50.5	13,900	6.38	29.2	13,700	5.37
100	18,000	8.32	73.2	14,500	6.95	45.2	14,400	6.03
			93.2	14,200	6.83	62.3	14,700	6.57
			100	13,800	6.63	71.3	14,800	7.12
						94.8	14,300	6.97
						100	13,800	6.63
Acetone-Nitrobenzene.			Acetone-Benzene.					
Ph·NO <sub>2</sub> , wt. %.	$E$ .	$\log PZ$ .	COMe <sub>2</sub> , wt. %.	$E$ .	$\log PZ$ .			
0	14,000	6.49	0	14,400	5.55			
25.3	14,300	6.80	22.9	13,900	5.96			
53.4	14,300	6.92	69.2	14,000	6.44			
77.5	14,400	7.08	100	14,000	6.49			
100	13,800	6.63						

*Discussion.*—Fig. 1 shows the variation of activation energy with composition for four systems. The system benzene-nitrobenzene, which is not plotted, closely resembles that of *isopropyl ether-nitrobenzene*. The remaining figures show the variations of  $\log PZ$ , which are generally similar to those of  $E$ .

To reduce the  $\log PZ$  values to correspond to a standard activation energy the following procedure was adopted. The form of the correlation between  $E$  and  $\log PZ$  was assumed to be that discussed in the previous paper, namely  $d \log PZ / d(1/E^{\frac{1}{2}}) = \text{constant}$ . From the results of that paper the constant was taken to be approximately  $-0.22 \times 10^4$ . The value of  $E$  for pure nitrobenzene, 13,800, was taken as an arbitrary standard, and the observed values of  $\log PZ$  were recalculated to what they would have been, according to the

formula, had the activation energies all been 13,800. The reduced values are shown plotted against composition in the diagrams (broken lines).

In each of the cases where a polar solvent is added to a non-polar solvent, the reduced values show a steady increase, and lead to curves of very similar form. Where two highly polar solvents are mixed, as with the system acetone-nitrobenzene, the reduced values of  $\log PZ$  are almost constant.

With regard to the possible explanation of this increase of  $PZ$  with solvent, several factors may contribute. In the first place, the reduced variations are now of limited range and not outside conceivable variations in the actual encounter numbers. Secondly, if a ternary collision with a solvent molecule is necessary to stabilise the activated polar product and prevent its reversion into its components, then polar solvents may well be supposed to be more efficient in this respect. The same results would be achieved if the polar solvent molecules shortened the time which, according to the theory discussed in the previous paper, elapses on the average between activation and reaction.

We are not primarily concerned in this paper with the actual relations between the activation energy itself and the composition, but the curves in Fig. 1 call for the following remarks. The **S**-shaped curve is found in systems containing nitrobenzene and a non-polar solvent, but not in the system nitrobenzene-acetone, where a single maximum occurs. On the other hand, when acetone is added to benzene there is initially a sharp fall. If the initial fall is regarded as characteristic of the addition of a polar solvent to a non-polar one, then the **S**-shaped curves are probably to be interpreted as a superposition of the two types.

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