294. *The Functional Relation between the Constants of the Arrhenius Equation: The Formation of a Series of Quaternary Ammonium Salts in Benzene–Nitrobenzene Mixtures.*

By H. C. Raine and C. N. Hinshelwood.

Among the results of recent investigations dealing with the kinetics of reactions in solution are the following:

(*a*) Two important terms in the activation energy are the work required to bring an attacking reagent up to the reactive centre and that required to extend bonds which must be broken in the reaction. The relative values of the two terms vary considerably from reaction to reaction. This variation is in evidence in the series constituted by the interaction of methyl iodide and *iso*propyl iodide respectively with triethylamine and with pyridine.

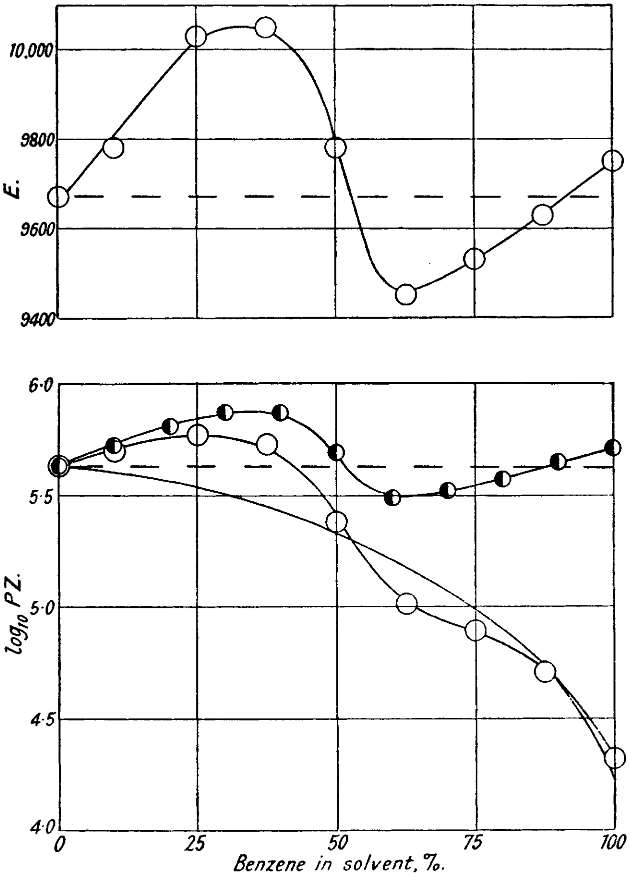
(*b*) There is not infrequently a correlation between the two constants E and log PZ of the Arrhenius equation: the conditions under which this occurs have not been fully worked out. A well-marked example of it is found with the reaction between pyridine and methyl iodide in a range of benzene–nitrobenzene mixtures as solvents: E varies in a very characteristic manner with solvent composition and log PZ shows an unmistakable tendency to follow it.

The object of the experiments was to find out whether there is any connection between the two sets of facts (*a*) and (*b*): whether, for example, the correlation is more in evidence when the activation energy is mainly needed for the stretching of bonds. All four reactions mentioned in (*a*) have therefore been compared in respect of the correlation of E and log PZ. A method has been devised for making quantitative comparison of the degree of correlation, and the results show that the differences between the four reactions are not great. Such differences as there are do not lend

support to the idea that the correlation is most in evidence when the activation energy is chiefly concerned with bond extension, but rather the reverse. The meaning of this result is discussed, and the nature of the log *PZ*–*E* correlation in general is further considered.

WHEN the activation energy for the reaction between methyl iodide and pyridine in benzene–nitrobenzene mixtures is plotted against the composition of the solvent the curve obtained has a characteristic shape with a maximum and minimum (Fairclough and Hinshelwood, J., 1937, 1573). The corresponding variations in the temperature-independent factor, log *PZ*, of the Arrhenius equation can be analysed into two factors, one a regular increase with the polarity of the solvent and the other a well-defined correlation with the activation energy itself. This kind of correlation has frequently been found in other types of reaction. Among other possible causes for it is the following (Fairclough and Hinshelwood, J., 1937, 538) : increased activation energy may be due to increased strengths of certain bonds; this extra strength is associated with a greater frequency, so that the time required by the activated complex to complete its rearrangement may be less. Under certain conditions the result may be a greater probability of reaction in the way required.

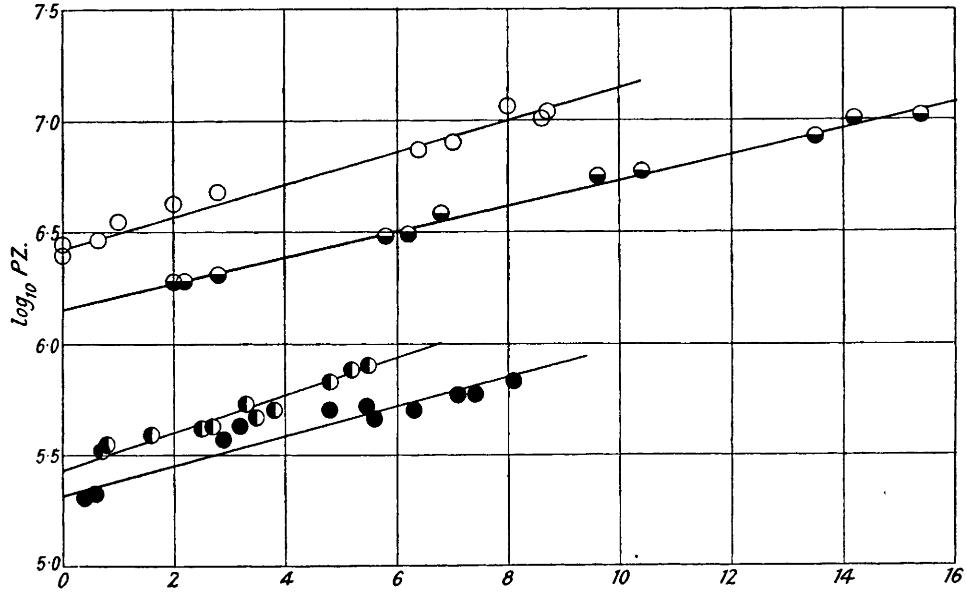
FIG. 1.



Bond strengths are not the only factors determining activation energies (Evans and Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11). The work needed to bring up the attacking reagent to the reactive centre may be still more important. In the formation of quaternary ammonium salts the influence of substituents follows their expected effect on the repulsion to be overcome; but the relative importance of the bond stretching varies from reaction to reaction. From the fact that there is little difference between the activation energies of the reactions of *iso*propyl iodide with pyridine and with triethylamine, it may be concluded that the activation of the alkyl–iodine bond is more important than in the reactions of methyl iodide with the same bases, where the difference in E is great (Hinshelwood, Laidler, and Timm, J., **1938**, 848).

It seemed of interest to find out whether the degree of correlation between E and log PZ with variation of solvent composition showed any regular trend with the shift in the relative importance of the bond strength and repulsion energy in the series : methyl iodide–triethylamine, methyl iodide–pyridine, *iso*propyl iodide–triethylamine, *iso*propyl iodide–pyridine.

FIG. 2.



○ *Formation of methylpyridinium iodide.*
◒ *Formation of* iso*propylpyridinium iodide.*
◐ *Formation of methyltriethylammonium iodide.*
● *Formation of triethyl*iso*propylammonium iodide.*

For convenience of representation certain lines have been displaced along the E *axis.*

The values of E and log PZ have therefore been determined for the three of these pairs not previously studied : the solvents were the complete range of benzene–nitrobenzene mixtures previously used for pyridine and methyl iodide.

The experimental methods were as described in earlier papers (Laidler and Hinshelwood, J., **1938**, 858). The results are tabulated below. The method of treating them was as follows.

The activation energy varies with solvent composition according to an **S**-shaped curve (Fig. 1). There are two compositions for which E has the same value as for pure nitrobenzene. Any differences between the corresponding values of log PZ cannot be due to correlation with E, but represent what has been called the polarity effect. The three values of log PZ when plotted against solvent composition yield a curve which is little enough removed from a straight line to make interpolation relatively easy, provided we permit ourselves to make the assumption that the polarity effect is representable at all by a curve of simple form. An example of such an interpolation curve is shown in Fig. 1 by the line without circles. The corresponding curve for the total variation in log PZ is shown by the curve with open circles. For each composition the observed value of log PZ is corrected for the change which would be due to the polarity effect operating alone. The curve with the half-black circles is the resultant of the two other curves constructed by algebraic addition. It is seen to be closely similar in shape to the curve obtained by plotting E against composition. The corrected values of log PZ are plotted against the corresponding values of E for the four reactions in Fig. 2. In the first place it is seen that the relation is linear in each case within the limit of experimental error. Secondly, it appears that the differences in slope are not considerable. Thirdly, however, it is evident that the small differences which occur are in the sense that makes the degree of correlation least when the influence of the bond strength might be expected to be greatest.

The slopes of the four lines are :

Triethylamine and methyl iodide	$7{\cdot}06 \times 10^{-4}$
Triethylamine and *iso*propyl iodide	$6{\cdot}77 \times 10^{-4}$
Pyridine and methyl iodide	$6{\cdot}45 \times 10^{-4}$
Pyridine and *iso*propyl iodide	$5{\cdot}60 \times 10^{-4}$

TABLE I.

Solvent.*	Temp.	$k \times 10^3$.	Solvent.*	Temp.	$k \times 10^3$.	Solvent.*	Temp.	$k \times 10^3$.
		The Reaction between Triethylamine and Methyl Iodide.						
I	5·3°	10·7	IV	4·0°	5·72	VII	4·0°	2·20
	15·0	20·1		15·0	12·0		15·0	4·30
	25·0	33·5		25·0	22·9		25·0	7·75
	40·0	76·1		40·1	46·7		40·1	15·5
IIa	4·0	9·27	V	4·6	4·40	VIII	15·0	2·43
	15·0	17·9		15·0	8·02		25·0	4·57
	25·0	32·1		25·0	14·8		40·1	9·77
	40·0	70·8		40·1	34·1		60·1	25·1
III	4·7	7·05	VI	5·0	3·68	IX	15·0	0·827
	15·0	13·0		15·0	6·53		25·0	1·40
	25·0	24·4		25·0	11·5		40·1	3·23
	40·0	55·0		40·1	25·1		60·1	8·25
		The Reaction between Pyridine and iso*Propyl Iodide.*						
		$k \times 10^6$			$k \times 10^6$.			$k \times 10^6$.
I	40·0	4·08	IV	60·0	9·48	VII	60·0	2·83
	60·0	22·1		80·2	38·8		80·2	12·1
	80·0	91·2		99·6	157		99·9	42·5
	99·3	310		121·0	635		121·0	137
II	40·0	3·33	V	60·0	8·45	VIII	80·2	6·94
	60·0	18·5		80·2	30·4		100·1	23·4
	80·2	71·6		100·2	115		121·0	76·9
	100·1	295		121·0	414		138·7	220
III	60·0	12·0	VI	60·0	4·34	IX	99·6	8·04
	80·2	94·0		80·2	21·3		121·0	29·5
	99·7	210		100·0	76·1		138·9	81·0
	121·0	571		121·0	220		150·8	151
		The Reaction between Triethylamine and iso*Propyl Iodide.*						
		$k \times 10^5$.			$k \times 10^5$.			$k \times 10^5$.
I	60·1	2·61	IV	80·0	2·50	VII	99·8	1·51
	80·0	8·24		99·7	8·35		120·6	4·59
	100·0	30·6		120·6	24·3		139·0	10·2
	120·4	92·0		138·0	71·3		153·4	22·1
II	60·0	1·42		153·4	132	VIII	99·5	0·570
	80·0	5·74	V	80·2	1·68		120·0	1·86
	99·4	18·5		99·9	5·62		138·8	4·38
	120·0	58·8		120·0	19·6		153·2	8·25
III	80·0	3·95		139·5	48·9	IX	99·6	0·181
	99·7	13·2		153·4	82·3		120·3	0·620
	121·0	41·7	VI	99·2	2·81		138·4	1·39
	138·4	107		119·8	9·94		153·1	3·06
	153·4	205		139·1	23·9			
				153·5	45·9			

The constants are corrected for solvent expansion.

* See Table II.

The slope is least for the reaction between pyridine and *iso*propyl iodide, and greatest for triethylamine and methyl iodide. In the latter the repulsion energy appears to be most important; in the former, the bond energy.

This raises the question of the general interpretation of the *P–E* correlation. It appears in unimolecular reactions and can therefore presumably be connected with bond-breaking processes; and the form of the relationship can be plausibly enough accounted for by a theory based upon the idea of a parallelism between activation energy and bond strength. The present results, however, as far as they go, suggest a widening of the basis of the theoretical interpretation. This can easily be given in a form which includes the previous idea as a special case.

Suppose a reaction took place in some hypothetical ideal state with activation energy *E*, and the probability factor *P*. Now let the conditions be changed, *e.g.*, by the presence of solvent molecules, so that the value of *E* is lowered. The lowering is due either to the effect of one single factor or to the simultaneous co-operation of a number of factors. It is in the latter case that the correlation is to be expected, for each factor can be thought of as reducing *E* by an amount *e*, and if *n* factors co-operate the change is given by $\Delta E = ne$; but the chance that each of these factors is favourable at the moment of activation is less than unity, so that for *n* of them to be favourable at once the probability will be reduced in the ratio $P'/P = p^n$, where p is less than unity. Taking logarithms and eliminating *n*, we find that *E* and log *P* change in a parallel manner.

TABLE II.

Solvent.	C_6H_6.	$PhNO_2$.	*E*, cals.	log *PZ*.	Solvent.	C_6H_6.	$PhNO_2$.	*E*, cals.	log *PZ*.
The Reaction between Triethylamine and Methyl Iodide.					*The Reaction between Triethylamine and* iso*Propyl Iodide.*				
I	0	100	9,650	5·63	I	0	100	16,000	5·70
IIa	10	90	9,800	5·70	II	12·5	87·5	16,050	5·60
III	25	75	10,050	5·77	III	25	75	16,100	5·59
IV	37·5	62·5	10,050	5·73	IV	37·5	62·5	16,250	5·49
V	50	50	9,800	5·38	V	50	50	16,050	5·22
VI	62·5	37·5	9,450	5·01	VI	62·5	37·5	15,750	4·76
VII	75	25	9,550	4·89	VII	75	25	15,500	4·09
VIII	87·5	12·5	9,650	4·71	VIII	87·5	12·5	15,750	4·05
IX	100	0	9,750	4·32	IX	100	0	16,300	3·89
The Reaction between Pyridine and iso*Propyl Iodide.*					*The Reaction between Pyridine and Methyl Iodide.*				
I	0	100	16,700	6·31	—	0	100	13,800	6·63
II	12·5	87·5	17,200	6·57	—	6·8	93·2	14,200	6·83
III	25	75	17,600	6·65	—	26·8	73·2	14,500	6·95
IV	37·5	62·5	17,900	6·72	—	49·5	50·5	13,900	6·38
V	50	50	17,350	6·28	—	68·8	31·2	13,600	5·88
VI	62·5	37·5	16,900	5·77	—	91·65	8·35	13,700	5·32
VII	75	25	16,550	5·35	—	100	0	14,400	5·55
VIII	87·5	12·5	16,900	5·31					
IX	100	0	17,950	5·45					

The data for the reaction between pyridine and methyl iodide are those of Fairclough (B.Sc. Thesis, Oxford, 1937).

The statistical basis of this relation is essentially the same as that given in the earlier treatment of the special example depending on bond strength. In this theory, if the activation energy were lowered by weakening a bond, the vibration frequency became less, so that there was a longer interval between activation and the moment when the molecule reached the right internal condition to react; it was supposed that these would be deactivation or resolution of the active complex into its components except when it happened to have an exceptionally long life. The latter condition was supposed to depend on the favourable conjunction of a number of independent factors, and it was precisely this assumption which gave rise to the correlation of *E* with the logarithm rather than any algebraic function of *P*.

In unimolecular reactions (Fairclough, J., 1938, 1186; Wiig, *J. Physical Chem.*, 1928, **32**, 961), such as the decarboxylation of the ions of the aliphatic acids, we probably have to deal with a mechanism in which the activation energy is required chiefly for the breaking of bonds. Here the idea that the activated molecules react only if a number of factors have ensured them an abnormally long period free from disturbance by solvent molecules may well be correct.

In heterogeneous reactions a favourable geometrical and energetic relation between the adsorbed molecule and several molecules of the solid catalyst may be needed : the correlation may then appear.

The correlation is always much in evidence when we have to deal with change of solvent. Here we may suppose that a favourable disposition, achieved by chance, of a number of solvent molecules round the reacting partners lowers the activation energy by facilitating approach, that is, by reducing what we have called the repulsion energy. The probability however is correspondingly lowered. This may well be the state of affairs in the systems studied in the experimental part of this paper.

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