## 271. *The Factors determining the Velocity of Reactions in Solution. The Formation of Quaternary Ammonium Salts in Benzene Solution.*

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The speed of a chemical reaction may be expressed in the form $PZe^{-E/RT}$, where $Z$ is the collision number, $E$ the activation energy, and $P$ a probability factor nearly independent of temperature. The magnitude of $P$ varies over a very wide range, being of the order $10^{-8}$ for some bimolecular reactions and of the order unity for others (for references, see this vol., p. 587). We may expect to obtain some information about the relative importance of $P$ and $E$, and about the cause of the wide variation in $P$, by studying a series of related reactions. The reaction between tertiary amines and alkyl halides, of the general type $R_3N + R'X = R_3R'NX$, is a suitable bimolecular reaction for the purpose. It was studied first by Menschutkin (*Z. physikal. Chem.*, 1890, **6**, 41), and frequently since, but the available data are not of the kind necessary for a systematic investigation of the relations of $P$ and $E$ to the structures or polarities of the reacting molecules. Accordingly, we have made a study of the variations of $E$ and $P$ when the nature of the tertiary base, of the halogen atom, or of the alkyl group in the halide is changed.

Measurements have been made for 12 reactions, with benzene as solvent, at a series of temperatures. The experimental method was essentially that of Menschutkin, the reactants being sealed up in small glass tubes and heated in thermostats (electrically controlled baths, specially constructed boiling-liquid thermostats, or cryostats in Dewar vessels). The progress of the reaction was followed by estimation of the ionisable halogen (Volhard method). With benzene as solvent, no difficulty was found with the titration, since the alkyl halide stayed in the benzene, and the ionisable halide readily passed into the aqueous layer. " Analar " benzene was employed, and the various reactants were fractionated to constant b. p. in an all-glass apparatus. Solutions were made by weight, and were usually $N/5$ before mixing, or $N/10$ in the actual reacting system, since equivalent quantities were always used. The temperatures were standardised by N.P.L. thermometers.

Velocity constants were corrected for the expansion of the solvent with temperature.

The numbers in Table I illustrate the type of bimolecular constant found; $t$ is the time in minutes, $x$ the % change, and $k'$ the bimolecular constant (g.-mol./l./sec.), uncorrected for the expansion of the solvent; $a$ is the initial concentration of amine and of halide.

TABLE I.

Pyridine and ethyl iodide at 100°; $a$ = 0·10.

| $t$. | $x$. | $k \times 10^4$. |
|---|---|---|
| 179 | 12·0 | 1·27 |
| 420 | 24·0 | 1·25 |
| 737 | 35·0 | 1·22 |
| 1054 | 44·5 | 1·27 |
| 1530 | 53·0 | 1·22 |
| 2497 | 65·5 | 1·27 |
| 4020 | 75·0 | 1·24 |

Trimethylamine and *n*-propyl bromide at 139·4°; $a$ = 0·10.

| $t$. | $x$. | $k \times 10^3$. |
|---|---|---|
| 13 | 11·2 | 1·62 |
| 34 | 25·7 | 1·70 |
| 59 | 36·7 | 1·64 |
| 120 | 55·2 | 1·71 |

Trimethylamine and methyl iodide at 4·4°; $a$ = 0·01667.

| $t$. | $x$. | $k \times 10^3$. |
|---|---|---|
| 22 | 13·8 | 7·3 |
| 34 | 18·0 | 6·5 |
| 53 | 24·3 | 6·1 |
| 73 | 30·3 | 6·0 |
| 170 | 50·5 | 6·0 |

TABLE II.

Pyridine and ethyl iodide.

| Temp. | $k \times 10^5$. |
|---|---|
| 80·5° | 4·17 |
| 99·7 | 13·8 |
| 118·2 | 32·7 |
| 139·3 | 107 |

Triethylamine and methyl iodide.

| Temp. | $k \times 10^4$. |
|---|---|
| 4·4° | 4·35 |
| 13·5 | 8·13 |
| 25·0 | 15·4 |
| 40·0 | 32·1 |

Pyridine and methyl iodide.

| Temp. | $k \times 10^5$. |
|---|---|
| 40·1° | 3·38 |
| 80·5 | 52·4 |
| 99·6 | 131 |
| 117·2 | 328 |

Pyridine and *iso*propyl iodide.

| Temp. | $k \times 10^6$. |
|---|---|
| 80·6° | 2·68 |
| 99·7 | 10·0 |
| 117·7 | 30·3 |
| 139·4 | 124 |

Trimethylamine and methyl iodide.

| Temp. | $k \times 10^3$. |
|---|---|
| 4·4° | 6·00 |
| 16·0 | 11·5 |
| 25·0 | 18·5 |
| 40·1 | 37·1 |

Pyridine and *n*-propyl bromide.

| Temp. | $k \times 10^6$. |
|---|---|
| 80·6° | 2·82 |
| 99·7 | 10·1 |
| 117·7 | 25·0 |
| 139·4 | 78·2 |

Quinoline and methyl iodide.

| Temp. | $k \times 10^4$. |
|---|---|
| 80·5° | 1·21 |
| 99·8 | 3·62 |
| 119·2 | 9·10 |
| 139·4 | 15·7 |

Pyridine and *n*-propyl iodide.

| Temp. | $k \times 10^5$. |
|---|---|
| 80·6° | 1·47 |
| 99·7 | 4·84 |
| 117·7 | 12·3 |
| 139·4 | 39·6 |

Pyridine and ethyl bromide.

| Temp. | $k \times 10^6$. |
|---|---|
| 80·5° | 7·25 |
| 99·8 | 24·9 |
| 118·5 | 68·5 |
| 139·4 | 210 |

Trimethylamine and *n*-propyl bromide.

| Temp. | $k \times 10^4$. |
|---|---|
| 80·5° | 1·78 |
| 99·7 | 4·26 |
| 117·6 | 8·76 |
| 139·4 | 19·6 |

Trimethylamine and ethyl iodide.

| Temp. | $k \times 10^4$. |
|---|---|
| 25·0° | 2·12 |
| 40·1 | 5·26 |
| 80·6 | 43·9 |

Trimethylamine and *n*-propyl iodide.

| Temp. | $k \times 10^4$. |
|---|---|
| 40·0° | 1·20 |
| 80·6 | 9·95 |
| 99·7 | 21·9 |

In Table II are given the velocity constants for the various temperatures, all corrected for expansion of solvent. In all cases the Arrhenius equation is satisfactorily obeyed.

### *Discussion of the Results.*

The most convenient way of representing the results is to plot log $k$ for a given temperature against $E$. If for two reactions the difference in velocity is due entirely to a difference in $E$, then the line joining the two corresponding points on the diagram will have the slope 2·303$RT$, which it will be convenient to call the standard slope. If the line is steeper than this, then the value of $P$ is greater for the slower reaction, while if the line is less steep it is smaller. By reading off the distance of any point from a line of the standard slope passing through another point, one can see at a glance how much of the change in velocity has been due to the change in $E$ and how much to that in $P$.

In Table III are tabulated the values of $E$ and of $\log_{10} k_{100}$, for all the reactions studied, together with the values for the reaction of triethylamine and ethyl iodide in benzene (Grimm, Ruf, and Wolff, *Z. physikal. Chem.*, **1931**, *B*, **13**, 299). The significant facts revealed by these results may be stated as follows.

The most important factor determining the variation in velocity (which covers a

$10^4$—$10^5$-fold range) is the energy of activation. If all the results are plotted on a single diagram, there is evident a well-defined tendency for the points to group themselves in the neighbourhood of a line of the standard slope.

FIG. 1.

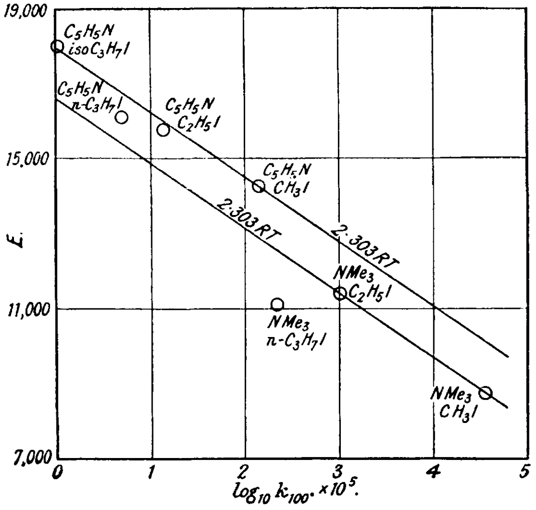


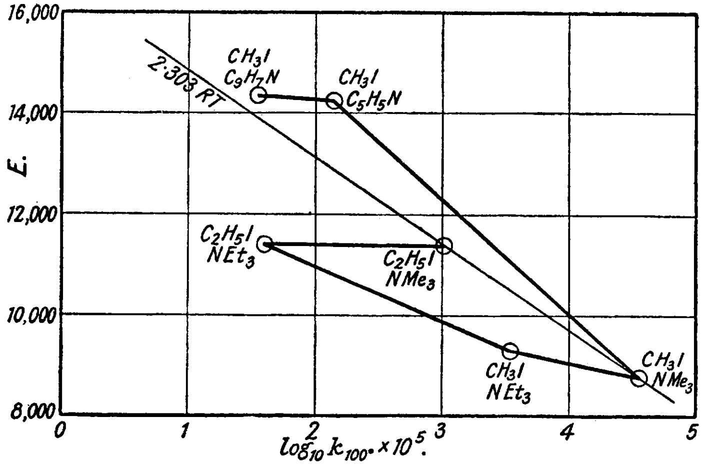
TABLE III.

| Base. | Halide. | 5 + $\log_{10} k_{100°}$. | *E*. |
|---|---|---|---|
| $NMe_3$ | MeI | 4·56 | 8,790 |
| $NEt_3$ | MeI | 3·55 | 9,300 |
| $NMe_3$ | $Pr^{\alpha}I$ | 2·35 | 11,200 |
| $NMe_3$ | EtI | 3·01 | 11,400 |
| $NEt_3$ | EtI | 2·60 | 11,400 |
| $NMe_3$ | $Pr^{\alpha}Br$ | 1·63 | 11,700 |
| $C_5H_5N$ | MeI | 2·15 | 14,250 |
| $C_9H_7N$ | MeI | 1·55 | 14,350 |
| $C_5H_5N$ | EtI | 1·14 | 15,760 |
| $C_5H_5N$ | $Pr^{\alpha}Br$ | 0·00 | 15,900 |
| $C_5H_5N$ | $Pr^{\alpha}I$ | 0·69 | 16,100 |
| $C_5H_5N$ | EtBr | 0·39 | 16,200 |
| $C_5H_5N$ | $Pr^{\beta}I$ | 0·015 | 18,000 |

Thus we may say that the low value of *P*, which is of the order $10^{-6}$—$10^{-8}$, is a characteristic of all the reactions of the general type we are studying.

Nevertheless, there are certain definite regularities detectable in the changes of *P* produced by varying one or other of the reacting substances. Although these variations are not great in comparison with the total range of variation of the reaction velocity, it may be useful to consider them carefully, since their relation to the structures or polarities of the reacting molecules may, at least, give important indications of the factors upon which the absolute magnitude of *P* depends in general.

FIG. 2.



(1) As shown by Fig. 1, the change in velocity on passing from the methyl halide to the ethyl halide is a matter principally of the activation energy. In passing further to the *n*-propyl halide, the change of activation energy is less important, but a marked fall in *P* occurs. These statements apply both to the reactions of pyridine and to those of trimethylamine. The fall in *P* on passing from the ethyl halide to the propyl halide is observed both for the iodides, as shown in Fig. 1, and also for the bromides, as shown in

Fig. 3. On passage from ethyl to *iso*propyl iodide there is a marked increase in *E* and no serious change in *P*.

(2) The decrease in reaction velocity between the aliphatic tertiary amine, trimethylamine, and pyridine is principally determined by the change in activation energy.

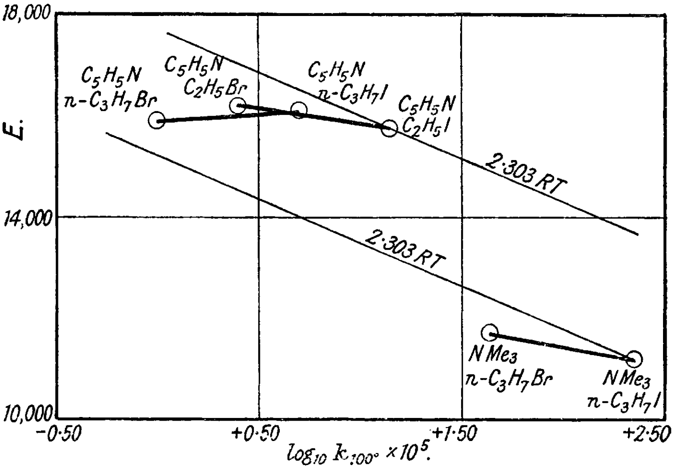
(3) On the other hand, the difference between trimethyl- and triethyl-amine is largely due to the change of *P*. This is shown in Fig. 2 for the reactions with both methyl iodide and ethyl iodide.

(4) On passing from pyridine to quinoline, there is a noticeable fall in *P*.

(5) Fig. 3 shows that the smaller speed of reaction of the bromides compared with the iodides is largely a matter of the smaller *P* value. This somewhat unexpected result is exemplified three times.

Taking the results as a whole, we suggest the following conclusions. There is a large fall in rate on passing from the aliphatic tertiary amines to pyridine. This is mainly due to the increase in energy of activation. The ease of reaction is evidently connected with the basic strength and the availability of the unshared electron pair of the nitrogen. Thus the energy of activation is the appropriate quantity by which to judge the reactivity of this electron pair. This conclusion is supported by the fact that changes in the reactivity of aniline with benzoyl chloride, due to substituents which change the basic strength of the amine, are also measured by the changes in the activation energy.

Fig. 3.



The fall in *P* on passing from pyridine to quinoline is definite, though not very great, and can easily be explained by geometrical considerations, the clumsy appendage formed by the second ring decreasing the probability of suitably orientated collisions.

There is no marked increase in activation energy between trimethyl- and triethylamine, and we may suppose that the change in the availability of the electron pair is not great. There is a definite fall in *P*. Once again, it seems not unreasonable to attribute this to a decreased probability of favourably orientated collisions, the lengthening of each of three hydrocarbon chains making favourable orientation more difficult.

In so far as the replacement of one alkyl group by another leads to changes in the strength of the carbon–halogen bond, we should expect changes in rate to be correlated with changes in activation energy. This is what is found for the methyl and ethyl compounds. On proceeding to the *n*-propyl compounds, it is not surprising that no further very marked increase in activation energy occurs, since successive additions to a chain usually have less and less effect. The definite falling in *P* which now occurs is parallel with that found on going from the methyl- to the ethyl-amine, and may be the result of adverse geometrical conditions caused by the longer chain. That this makes itself felt between methyl and ethyl with the amines, and only between ethyl and propyl with the halides, may easily be accounted for by the fact that in the former case there are three chains and in the latter one only. That the point corresponding to the *iso*propyl compound appears to lie more or less on the standard line may be due to the fact that the additional methyl group will exert a stronger polar influence on the iodine–carbon bond in *iso*propyl iodide than it can in the *n*-compound. Thus it influences the activation energy more effectively.

The influence of the nature of the halogen atom on $P$ is in some respects the most interesting of the results. The decrease on replacing iodine by bromine, although not very great, is definite and consistent. It cannot be accounted for by a change in the collision frequency, which would indeed be slightly greater for the bromides, nor is it likely that the somewhat smaller size of the bromine can account for the effect in a geometrical way. It seems rather that there is some quality of the iodine atom which makes a favourable energy transfer on collision more probable than with bromine, leading more often to a direct critical activation of the molecule. Some such property as the polarisability of the iodine may be concerned, but without deciding that question, we may still point out the analogy between the effect now observed and the great efficiency of iodine molecules in catalytic collisions with aldehyde molecules in gas reactions. If this point of view is a correct one, it gives a significant indication of the conditions which determine whether $P$ in general is great or small. There must be a mutual interaction of the colliding molecules favouring such an energy transfer that immediate critical activation of the molecule is possible (see this vol., p. **1111**). This condition will naturally be modified to some extent by any change whatever in the nature of the reacting molecules, and so may be superposed on any of the factors considered earlier in this discussion. A separation of the various influences into quite independent factors is naturally to some extent arbitrary.

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