## 338. *The Reactivity of Halogen Compounds. Part III. The Velocities of Reaction, Energies of Activation, and Probability Factors for the Reaction between* 2 : 4-*Dinitrobromobenzene and some Aromatic Primary Amines.*

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RHEINLANDER (J., 1923, **123**, 3099) found that the ratio of the velocity constants of the reactions of aniline with 1-bromo- and with 1-chloro-2 : 4-dinitrobenzene was approximately 1·5 : 1, a much smaller ratio than that usually observed with aliphatic bromo- and chloro-compounds (cf. Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589). It is obviously of interest to determine whether the cause of this difference is to be found in the energy of activation or in the probability factor. We have recently obtained the velocity constants, energies of activation, and probability factors for the reaction between 1-chloro-2 : 4-dinitrobenzene and a number of aromatic primary amines (*J. Physical Chem.*, in the press) and now report the results for aniline and *m*- and *p*-toluidine with 1-bromo-2 : 4-dinitrobenzene. The following table summarises both sets of experiments :

1-*Halogeno*-2 : 4-*dinitrobenzene and aromatic primary amines in ethyl-alcoholic solution.*

[Bromo-compound] = 0·1$M$ ; [Base] = 0·4$M$, except where otherwise stated.

| Base. | $k_{35^\circ}$. | $k_{45^\circ}$. | $E$. | log $A$. | log $P$. |
|---|---|---|---|---|---|
| Aniline | 0·01037 | 0·0185 | 11,220 | 6·0 | 5·5 |
| ,, (0·8$M$) | 0·00964 | — | — | — | — |
| *m*-Toluidine | 0·01385 | 0·02525 | 11,640 | 6·4 | 6·0 |
| *p*- ,, | 0·0319 | 0·0552 | 10,630 | 6·0 | 5·4 |
| Former data for chloro-compound. | | | | | |
| Aniline | 0·00691 | 0·0123 | 11,180 | 5·8 | 5·3 |
| ,, (0·8$M$) | 0·00649 | — | — | — | — |
| *m*-Toluidine | 0·00975 | 0·0177 | 11,560 | 6·2 | 5·7 |
| *p*- ,, | 0·0213 | 0·0357 | 10,060 | 5·4 | 5·0 |

Time is expressed in minutes; log $A$ is the quantity in the equation $k_T = Ae^{-E/RT}$; log $P$ is calculated as described by Williams and Hinshelwood (J., 1934, 1079).

The ratios of the rates of reaction with the bromo- to those with the chloro-compound are: aniline and *p*-toluidine, 1·5; *m*-toluidine, 1·4. If the change in velocity constant were due entirely to a change in $E$, then the fall in $E$ for the bromo-compound would be about 240 cals., well within the limits of experimental error. It may, however, be significant that in the three cases, instead of a fall, a rise in $E$ is observed; unless there is some constant error it would appear that the true energy of activation of the bromo-compound is unlikely to be less than that for the chloro-compound in all three cases, and that therefore the difference in rate of reaction is partially, and possibly wholly, due to a difference in probability factor.

The velocity constant for the reaction with the bromo-compound, as with the chloro-compound, falls with increasing amine concentration (cf. Rheinlander, *loc. cit.*). *p*-Toluidine reacts faster than *m*-toluidine, and the energies of activation are in the reverse order, as would be expected on the Lapworth–Robinson hypothesis (cf. Peacock, J., 1925, **127**, 2177). Both toluidines react faster than aniline (cf. Van Optall, *Rec. trav. chim.*, 1933, **52**, 901). Ingold and Shaw (J., 1927, 2918) found that toluene was nitrated in both the *p*- and the *m*-positions faster than was aniline, and this effect is apparently relayed to the attached nitrogen atom in the toluidines (cf. Waters, J., 1933, 1551).

The ethyl alcohol used was dried over quick-lime, fractionally distilled, and the middle fraction used. The bromodinitrobenzene was prepared in the ordinary way, and crystallised from ethyl alcohol. The aniline and *m*-toluidine were prepared by hydrolysis of the acetyl compounds. *p*-Toluidine was crystallised from light petroleum. The determination of the velocity constant was carried out as described by Rheinlander (*loc. cit.*), 50-c.c. glass-stoppered flasks being used for the reaction mixture.

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