339. *The Reactivity of Halogen Compounds. Part IV. The Effect of the Addition of Inactive Substances on the Rate of Reaction, Energy of Activation, and Probability Factor.*

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Williams and Hinshelwood (J., 1934, 1079) have shown that addition of nitrobenzene increases the rate of reaction between benzoyl chloride and aniline in benzene solution, and that its effect is proportional to its concentration. We have examined the effect of the addition of a number of inert substances—the term "inert" being used in a comparative sense—on the rates of reaction of 1-chloro- and 1-bromo-2 : 4-dinitrobenzene with aniline in ethyl-alcoholic solution. These experiments were carried out to test the suggestion (Peacock, *J. Physical Chem.*, 1926, **30**, 673) that the energy located in the benzene nucleus in aniline and similar compounds might serve as a reservoir of energy for the amino-group, increase the rate of reaction, and so explain the effect of change of concentration on reaction velocity; however, they do not support that view.

The measurements of velocity were carried out as described by Rheinlander (J., 1923, **123**, 3099). The tertiary bases used were all freed from primary or secondary bases by treatment with *p*-toluenesulphonyl chloride. In testing the effect of an added substance, a control experiment was always carried out with the same aniline, halogen compound, and absolute alcohol.

The solvent used was absolute alcohol (ethanol). The concentration of the halogeno-2 : 4-dinitrobenzene was 0·1*M*, and that of the aniline 0·4*M* except where otherwise stated; log *A* is derived from the equation $k = Ae^{-E/RT}$. Since the reactants are the same in any one series of experiments, Z_{AB} will be constant, and therefore log *A* is proportional to log *P*, where *P* is the probability factor. In the following tables are summarised the results of our experiments.

Effect of the addition of inert substances on the reactivity between aniline and 1-halogeno-2 : 4-dinitrobenzenes.

Substance added.	$k_{35°}$.	$k_{45°}$.	E.	log A.
1-Chloro-2 : 4-dinitrobenzene.				
Nil	0·00691	0·0123	11,180	5·8
Dimethylaniline, 0·4*M*	0·0058	0·01038	11,280	5·8
,, 0·8*M*	0·00449	0·00872	12,870	6·8
,, 1·6*M*	0·00326	0·00628	12,710	6·5
Benzene, 0·4*M*	0·0065	—	—	—
Chlorobenzene, 0·4*M*	0·0064	—	—	—
Nitrobenzene, 0·4*M*	0·0063	—	—	—
*cyclo*Hexane, 0·4*M*	0·00699	—	—	—
Nil (Aniline, 0·8*M*)	0·00649	—	—	—
1-Bromo-2 : 4-dinitrobenzene.				
Nil	0·01037	0·0185	11,220	6·0
Dimethylaniline, 0·4*M*	0·00858	0·0156	11,590	6·1
Methylethylaniline, 0·4*M*	—	0·0170	—	—
Diethylaniline, 0·4*M*	—	0·0174	—	—
Nil (Aniline, 0·8*M*)	0·00964	—	—	—

*cyclo*Hexane has no effect, which suggests that its inertness as a solvent is due, not so much to a deactivating effect, *i.e.*, a positive influence, as to something which it fails to do and other solvents do (cf. Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604). The effective substances all contain the benzene nucleus, which may be significant, for both the reactants also contain this nucleus. Dimethylaniline has the most marked effect: in 0·4*M*-concentration it lowered the velocity constant more than did the same concentration of aniline (cf. Peacock, *loc. cit.*). Its effect does not seem to be proportional to its concentration; it raises the value of the energy of activation, but the differences in E are, of course, liable to large experimental errors, probably of the order of 600 cals. The dipole moment of the substance added does not seem to be closely related to its effect.

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