

CCXCIII.—*The Velocity of Benzylation of certain Amines. Part II.*

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IN a previous paper (J., 1924, **125**, 1975), the energies of activation for the reaction between benzyl chloride and aniline or *p*-toluidine, and between *p*-nitrobenzyl chloride and aniline or *p*-toluidine were calculated from the velocity coefficients at two temperatures; no evidence was found that these energies are additive in character. The results of some further experiments are now described, but before their bearing on the nature of the process of activation is discussed the effect of substitution and other factors will be dealt with.

*m*-Nitrobenzyl chloride always reacted faster than *p*-nitrobenzyl chloride with the bases used. Olivier (*Rec. trav. chim.*, 1922, **41**, 646) obtained similar results in their hydrolysis. Slator and Twiss (J., 1909, **95**, 99) found that the order was reversed with sodium thiosulphate, where reaction is taking place with the negative thio-sulphate ion. These results can be explained on the alternate polarity hypothesis. With bases such as aniline and dimethylaniline nitrobenzyl chlorides react more slowly than does benzyl chloride, although it might be expected that the general polar effect of the nitro-group would make the chlorine more reactive in nitrobenzyl than in benzyl chloride. These results may be explained by assuming that before reaction occurs the base and the halogen compound combine loosely and the negative substituent in the benzyl chloride then weakens the tendency of the nitrogen to form part of a positive ion and so reduces the rate of reaction. The results of other experiments described below show that the introduction of a nitro-group into the nucleus of the base considerably reduces the reaction velocity.

Additional evidence in support of this assumption can be obtained from the results of Jones and Preston (J., 1912, **101**, 1931) and of Thomas (J., 1913, **103**, 595), who obtained the following velocity coefficients in alcohol at 40° with dimethylaniline: benzyl bromide 6.34, *m*-xylyl bromide 8.62, *p*-xylyl bromide 23.2, *p*-bromobenzyl bromide 6.03. The positively substituted benzyl bromide reacts faster, and the negatively substituted benzyl bromide more slowly, than the unsubstituted bromide.

The effect of substitution in the nucleus of the base upon the velocity coefficient can be seen from the data given later. *m*-Nitro-aniline reacts faster than *p*-nitroaniline, and *p*-toluidine faster than *m*-toluidine; results in accordance with the alternate polarity hypothesis.

The effect of concentration on the velocity coefficients and energies

of activation is sometimes considerable and, as will be seen from the tabulated results, depends on the character of the base employed. Attention is also directed to the difference in the effect of alteration in concentration upon the velocity and energy of activation of the reaction between benzyl chloride and dimethylaniline.

*Velocity coefficient and concentration.*

Base.	Conc.	Conc. of benzyl chloride.	$k_{35} \times 10^3$ .	$k_{45} \times 10^3$ .	$E$ , calories.
Aniline .....	0.4	0.2	3.62	8.5	16550
	0.8	"	3.68	9.2	17770
	1.6	"	4.07	10.55	18460
	1.6	0.4	4.25	11.2	18780
<i>o</i> -Toluidine .....	0.8	0.2		5.96	
	1.6	"		7.1	
<i>p</i> -Toluidine .....	0.8	"	5.96	14.7	17440
	1.6	"	6.21	15.1	17230
<i>p</i> -Chloroaniline .....	0.4	"		5.15	
	0.8	"		5.08	
Monoethylaniline.....	0.8	"		1.138	
	1.6	"		1.13	
Dimethylaniline .....	0.8	"	2.78	6.09	15210
	1.6	"	2.23	5.06	15890
Diethylaniline .....	0.8	"		0.400	
	1.6	"		0.303	

Examination of the results obtained showed also an interesting connexion between energy of activation and the constitution of the substituted benzyl chloride used. When the energies of activation of *m*- and *p*-nitrobenzyl chlorides with aniline, *p*-toluidine, *o*-toluidine, and dimethylaniline are compared, it is seen that, although there is apparently no strictly quantitative additive relation, there is a qualitative relationship, the energy of activation for *m*-nitrobenzyl chloride being less than that for *p*-nitrobenzyl chloride. The alternate polarity theory would lead us to expect that the chlorine in *m*-nitrobenzyl chloride should be more reactive than that in *p*-nitrobenzyl chloride. This conclusion is seen to be confirmed, not only by the velocity data, but also by the activation energy data. Applying the Bohr theory of atomic structure, it may be said that the displacement of electrons postulated by the alternate polarity theory decreases the amount of energy required to take an electron in the chlorine atom to its activated position.

*Energies of Activation in Methyl Alcohol.*

Base.	Benzyl chloride.	<i>m</i> -Nitrobenzyl chloride.	<i>p</i> -Nitrobenzyl chloride
Aniline .....	17770	17280	18030
<i>p</i> -Toluidine.....	17440	14480	17100
<i>o</i> -Toluidine .....	15420	14210	17680
Dimethylaniline.....	15210	13120	15960

The results described below also throw some light on the process of activation. The influence of a nitro-group in the benzyl chloride on the velocity of reaction is similar to the influence of a nitro-group in the nucleus of the amine. Also there is no evidence that, in general, the energy of activation is an additive property (Arrhenius, *Z. physikal. Chem.*, 1889, 4, 226). It is now suggested that the formation of a loose molecular complex precedes activation and the energy of activation measured in the cases cited is the energy of activation of such a complex.

### EXPERIMENTAL.

The method of estimation was that already described (*loc. cit.*). The constants were calculated by the modified equation, taking into account the base combined with the liberated hydrochloric acid; Moore, Somervell, and Derry (J., 1912, 101, 2459) have already directed attention to this omission in Menshutkin's calculations and their work should have been mentioned in the previous paper.

Tertiary bases gave much more constant values of the velocity coefficient than primary; difficulty was also experienced in getting concordant results with *p*-nitrobenzyl chloride. The bases used were crystallised as their hydrochlorides or acetyl compounds in the case of primary and secondary bases. The tertiary bases were tested for freedom from primary or secondary bases by the usual acetic anhydride test. The results are tabulated below.

#### *Velocity coefficients in methyl alcohol.*

Conc. of base, 0.8*M*. Conc. of chloride, 0.2*M*.

Base.	Temp. 45°.			Temp. 35°.		
	Benzyl chloride.	<i>m</i> -Nitro-benzyl chloride.	<i>p</i> -Nitro-benzyl chloride.	Benzyl chloride.	<i>m</i> -Nitro-benzyl chloride.	<i>p</i> -Nitro-benzyl chloride.
Aniline .....	0.0092	0.00451	0.00365	0.00368	0.00185	0.00144
<i>p</i> -Toluidine.....	0.0147	0.00874	0.00667	0.00596	0.00407	0.00276
<i>o</i> -Toluidine ...	0.00596	0.00256	0.00207	0.00269	0.00123	0.000832
Dimethylaniline	0.00609	0.00132	0.00092	0.00278	0.000671	0.000404

#### *Velocity coefficients at 35° and at 45°.*

(See also a preceding table).

Conc. of benzyl chloride, 0.2*M*.

*m*-Toluidine : conc. 0.8*M*;  $k_{35^\circ}$  0.00494.

*m*-Nitroaniline : conc. 0.8*M*;  $k_{45^\circ}$  0.00168.

*p*-Nitroaniline : conc. 0.4*M*;  $k_{45^\circ} > 0.0002$ .

Monomethylaniline : conc. 0.8*M*;  $k_{25^\circ}$  0.00644;  $k_{45^\circ}$  0.0187.

Monobenzylaniline : conc. 0.8*M*;  $k_{45^\circ}$  0.00335.

*p*-Bromodimethylaniline : conc. 0.8*M*;  $k_{45^\circ}$  0.00175.

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