CXVII.—*The Velocity of Formation of Quaternary Ammonium Salts from Trimethylamine and Benzyl Chloride and the Three Mononitrobenzyl Chlorides.*

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IT has been shown (J., 1926, 2863) that the relative order of the velocity of saponification of the isomeric methoxybenzoic esters and of ethyl benzoate is not the same in the two alcohol–water mixtures used as solvents. This behaviour appeared to be unusual and to require further investigation.

The choice of a suitable reaction which can be followed in a wide range of solvents is almost limited to the formation or decomposition of ammonium or sulphonium salts. The reaction selected was the formation of a quaternary ammonium salt from trimethylamine and a substituted benzyl chloride. The isomeric nitrobenzyl chlorides have been used by previous investigators and were deemed to be of interest for our present purpose.

Several workers have assumed that the effect of a substituent upon the velocity of reaction will depend upon the precise mechanism by which interaction takes place; this applies equally whether the effect be a general or an alternating effect. This assumption appears to be well illustrated by the behaviour of the alkyl and aryl halides with a number of reagents. It was pointed out by Slator (J., 1909, **95**, 100) that the results fell into at least two types when a comparison was made between the velocity coefficients of a series of reactions in which an organic halide was one of the reactants; thus the results with sodium ethoxide, sodium acetoacetate, and sodium thiosulphate showed great similarities. A second type of result was obtained with dissolved oxygen and with silver nitrate. The reaction with hydrolysing reagents gave results which differed in type from both the other classes. This division into types would appear to be true even when the comparison is drawn between three isomerides. The velocity coefficients for the reaction of the nitrobenzyl chlorides with a hydrolysing reagent (Olivier, *Rec. trav. chim.*, 1922, **41**, 646), with sodium thiosulphate (Slator, *loc. cit.*), and with potassium iodide (Conant, *J. Amer. Chem. Soc.*, 1925, **47**, 488) show this difference in type (Table I).

TABLE I.

			Relative values of k. Nitrobenzyl chlorides.		
Reagent.	Solvent.	Benzyl chloride.	*ortho.*	*meta.*	*para.*
Alkali.	Aq. alcohol.	22·6	1·06	1·28	1·00
Sodium thiosulphate.	,,	0·54	0·54	0·64	1·00
Trimethylamine.	,,	—	0·81	0·86	1·00
Potassium iodide.	Acetone.	0·14	1·32	0·57	1·00
Trimethylamine.	,,	0·98	0·55	0·80	1·00

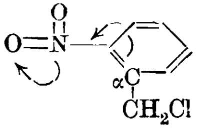
It is seen that on hydrolysis the benzyl chloride and the *m*-nitrobenzyl chloride have relatively higher velocity coefficients, whereas in the other reactions the *p*-nitrobenzyl chloride has the highest of these three. It would seem impossible to include the ortho-substituted halide in any generalisation, as the steric factor is variable and occasionally unexpected in its effects. A consideration of the results recorded in Tables I and II may be divided into two parts : first, the general effect of the nitro-group on the reactivity of the chlorine in the benzyl chloride molecule, and, secondly, the relative reactivities of the *o*-, *m*-, and *p*-nitrobenzyl chlorides.

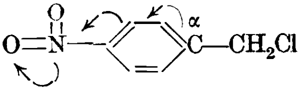
In connexion with the results obtained by Olivier (*loc. cit.*) for the hydrolysis of the nitrobenzyl chlorides, Robinson (J., 1926, 384) has suggested a mechanism based essentially upon the relative strengths of benzoic acid and the nitrobenzoic acids. Since the results obtained with potassium iodide, sodium thiosulphate, and trimethylamine differ so widely from those obtained on hydrolysis, it would appear that some other mechanism is involved.

To explain these results, the authors base their suggestions upon the relative strengths of the nitrophenols or of the nitrobenzoic acids as compared with the unsubstituted compounds. Since the substituted compounds have higher dissociation constants than the corresponding unsubstituted compounds, the general effect of the nitro-group is to give the benzene ring, as a whole, a higher affinity for a negative charge; further, they suggest that this attraction of electrons towards the nitro-group may proceed so far that the negative electronic attraction between the hydrogen and oxygen atoms may be converted into a positive repulsion between the nuclear charges of these atoms. In the event of dissociation, it is assumed that the valency electrons would be retained by the heavier nuclear charge of the oxygen atom, and the hydrogen would be thus liberated as a positive ion. If this conception is extended to the nitrobenzyl chlorides, it is seen that the nitro-group causes a movement of electrons towards itself and, as a consequence, repulsion of the nuclear charge of the chlorine atom may occur; there is, however, one essential difference, since, if the chlorine breaks away, it would be expected to do so as a negative ion, and this would necessitate the valency electrons of the carbon–chlorine union going with the chlorine atom. Thus the carbon–chlorine union in the nitrobenzyl chlorides is under a greater strain than that in the unsubstituted benzyl chloride, but this strain may be opposed by a second influence, since, if the chlorine is dissociated, the benzyl residue would become a positive ion which would be inconsistent with its greater affinity for a negative charge.

In the reactions with sodium thiosulphate and with potassium iodide, the product of the reaction is of a similar chemical nature to one of the reactants, and since no positive ion is formed by the benzyl residue, the difference in the velocity coefficients of the substituted and of the unsubstituted benzyl chlorides is to be ascribed to the strain on the carbon–chlorine union caused by the nitro-group. The reaction with trimethylamine is a special case, since in this reaction the chlorine is detached as a negative ion and the benzyl residue becomes part of the positive benzyltrimethylammonium ion, and the strain upon the carbon–chlorine union may be partly or completely neutralised by the resistance of the substituted benzyl residue to forming a part of this positive ion.

In a consideration of the alternating effect of the nitro-group, Robinson has shown (*loc. cit.*) that an electronic drift is caused in the direction of this grouping which may be represented as follows :





and that this drift will be most marked in the case of the *o*- and *p*-isomerides. Its effect will be to leave the carbon atoms marked α more positive than they were before the introduction of the nitro-group, and consequently the alternate effect will be in the same direction as the general effect.

In applying these considerations to groups other than the nitro-group, it was noted that, if the suggested electronic drifts of the general and of the alternate effects were in the same direction (*e.g.*, with the NH_2 and CH_3 groups), then

$$k_m > \text{or} < k_p \text{ according as } k_{\text{unsubs.}} > \text{or} < k_{\text{subs.}}.$$

In the case of the methoxy-group, the general effect is small and no generalisation is possible, and in the case of the halogens, the general and alternate effects are opposed.

Various views have been put forward to explain solvent effect; thus Cox (J., 1921, **119**, 142) suggested the formation of solvent–solute complexes, but Hawkins (J., 1922, **121**, 1170) was unable to obtain any evidence that such compounds exist. The effect due to the viscosity of the solvent has been examined by Buchböck (*Z. physikal. Chem.*, 1900, **34**, 229).

Arrhenius (*ibid.*, 1889, **4**, 226) was the first to suggest that molecules must be activated before they can enter into reaction. This energy of activation has more recently been ascribed to radiation (Lewis, J., 1914, *et seq.*) and to molecular collisions between the reacting molecules (Hinshelwood, *Phil. Mag.*, 1926, **2**, 360). The authors suggest that in the case of a reaction taking place in solution, the solvent itself activates the reacting molecules by means of its external electrical field. It is impossible to obtain a measure of this, as it is not completely expressed by the dielectric constant, by the chemical reactivity, or by the solvent power. It

TABLE II.

(*p*-Nitrobenzyl chloride, $k = 1$.)

Solvent.	Benzyl chloride.	Nitrobenzyl chlorides.	
		ortho.	*meta.*
Ethyl acetate	0·62	0·42	0·79
Acetone	0·97	0·55	0·80
Benzene	1·02	0·68	0·74
Ethyl benzoate	1·08	0·63	0·72
Anisole	1·32	0·70	0·71
Nitrobenzene	1·45	0·67	0·68
Ethyl alcohol	—	0·69	0·87
94·45% Alcohol–Water	—	0·69	0·85
Acetonitrile	—	0·79	0·87

might be expected that the presence of such groupings as an ethylenic linking, or of such elements as nitrogen, oxygen, or the halogens in a solvent would tend to increase the power of the solvent as an activating agent. The results recorded in Table II are in accord with these views. That the polarising action of the solvent is not its only effect, however, is shown in Table III, in which the columns headed 1, 2, 3, and 4 give respectively the relative reaction coefficients for the addition of trimethylamine to *p*-nitrobenzyl chloride, of ethyl iodide to triethylamine, of aniline to bromoacetophenone, and of allyl bromide to pyridine.

TABLE III.

Solvent.	1.	2.	3.	4.
Hexane	1	0·46	—	—
Ether	1·8	—	14	—
Benzene	17	17	17	17
Ethyl alcohol	108	94	680	136
Benzyl alcohol	298	332	510	—
Methyl alcohol	298	130	1020	—
Acetone	497	149	340	289
Nitrobenzene	1060	—	170	731
Acetophenone	890	—	—	595

Further consideration of the results given in Table II shows that the first six solvents stand in the order in which they decrease the value of the ratios k_m/k_p, k_p/k_o, and of $k_{\text{subs.}}/k_{\text{unsubs.}}$. These regularities are capable of explanation if it is assumed that the solvent has the power to increase or decrease the effect of the nitro-group on the halogen atom. In the ratios k_m/k_p and k_p/k_o, which depend upon the alternating effect of the nitro-group, the solvents in the given order increase the electronic drift, and since this is more powerful in the *p*- than in the *m*-position, the ratio k_m/k_p decreases.

The given range of solvents appears to influence the general effect in exactly the opposite order. Thus a range of solvents increasing the velocity of interaction of the *p*-nitrobenzyl chloride relatively to the *m*-isomeride should increase $k_{\text{subs.}}$ relatively to $k_{\text{unsubs.}}$, whereas the ratio decreases. Alcohol, acetonitrile, and anisole show yet a third effect of the solvent in that the ratios k_m/k_p and k_o/k_p are increased by these three solvents.

Dimroth (*Annalen*, 1910, **377**, 131) showed that the effect of solubility of the reactant in an intramolecular change was represented by $k \propto 1/S$, where k is the velocity coefficient and S the solubility of the starting product. It was shown that in the reaction between trimethylamine and *p*-nitrobenzyl chloride the relationship $k \propto 1/S_1S_2$ was not true (von Halban, *loc. cit.*). It appeared of interest to test the formula for the *meta/para* and *ortho/para* ratios of the nitrobenzyl chlorides. The relationship becomes $(k_m/k_p)(S_m/S_p) = \text{const.}$, since the solubility of the amine cancels out. It will be seen from Table IV that, even when the solubility ratios vary over a range of 50% and the velocity ratios over a similar range, no constant could be obtained.

TABLE IV.

	m/p Ratios.			*o/p* Ratios.		
Solvent.	100 k_m/k_p.	S_m/S_p.	Product.	100 k_o/k_p.	S_o/S_p.	Product.
Benzene	74	—	—	66·1	4·09	270
Ethyl acetate	78·7	5·65	490	41·8	3·69	154
Acetone	80·1	5·08	410	55·5	3·41	189
Ethyl benzoate	72·4	5·19	375	63·2	3·34	211
Nitrobenzene	68	4·78	325	67	3·18	212
Alcohol	86·6	3·79	320	69·5	3·20	222

EXPERIMENTAL.

The *o*- and *m*-nitrobenzyl chlorides were Kahlbaum products; the *p*-nitrobenzyl chloride was prepared by the nitration of benzyl chloride according to the method of Beilstein (*Annalen*, 1866, **139**, 337). The solvents acetone, acetonitrile, and anisole were B.D.H. products; the ethyl acetate, ethyl benzoate, and nitrobenzene were prepared in the usual manner. The trimethylamine was stored as the hydrochloride, from which the free amine was liberated, as required, by warming with concentrated aqueous potassium hydroxide. The gas was dried by passing through a series of soda-lime tubes, and absorbed immediately in the freshly-distilled solvent. The solution was standardised by titration against hydrochloric acid, a mixture of methyl-orange and sodium indigotinsulphonate being used as indicator.

The reaction was carried out in sealed tubes, each containing 10 c.c. of the amine and 10 c.c. of the chloride solution. The tubes were filled, drained, and sealed whilst immersed in an ice-bath. Zero time was assumed to be the moment at which the tubes were placed in the thermostat, which was at 30° ± 0·1°. Usually seven tubes were used for each determination.

The ionisable chlorine was estimated gravimetrically. The tube was smashed under alcoholic silver nitrate and the solution diluted with water. This procedure ensured that all the quaternary ammonium chloride reacted with the silver nitrate, as it was found that with such solvents as nitrobenzene a mere shaking with aqueous silver nitrate was insufficient for a quantitative extraction. A slight modification was necessary in the experiments in which benzyl chloride was used: the tube was opened under water and the mixture shaken with benzene to remove unchanged benzyl chloride; the benzene was washed with small volumes of water, the wash-waters were added to the aqueous layer, and excess of silver nitrate was added. The silver chloride precipitates were weighed in a series of Gooch crucibles.

The solubilities of the nitrobenzyl chlorides (Table VIII) were determined by weighing solvent and solute into small bulbs, sealing off, and heating with shaking until solution was complete. The first reading was usually rejected; the succeeding three or four agreed within 0·1°, and this temperature was accepted as that of solution. Five determinations, with varying weights of solvent, were used in constructing a curve from which the solubility at 30° could be read off.

In the Tables V—VII, a represents the concentration of amine and b that of the benzyl or nitrobenzyl chloride expressed in g.-mol./litre.

TABLE V.

Benzyl chloride and trimethylamine in acetone.

$a = 0{\cdot}1362$; $b = 0{\cdot}1101$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^4$.
73	0·1350	0·0471	698
90	0·1514	0·0528	691
135	0·1873	0·0653	695
178	0·2077	0·0725	692
210	0·2221	0·0775	685
244	0·2330	0·0813	685
310	0·2548	0·0889	702
		Mean	692

TABLE VI.

m-Nitrobenzyl chloride and trimethylamine in acetonitrile.

$a = 0{\cdot}09377$; $b = 0{\cdot}04490$.

Time (mins.).	Wt. of AgCl.	x.	$k \times 10^3$.
63	0·0670	0·0234	146
70	0·0717	0·0250	146
80	0·0765	0·0267	145
100	0·0844	0·0294	142
113	0·0887	0·0310	141
124	0·0927	0·0324	142
		Mean	143

It was found that the quaternary ammonium salts were almost insoluble in benzene, ethyl acetate, and ethyl benzoate, slightly soluble in acetone, and easily soluble in nitrobenzene.

TABLE VII.

Benzyl chloride and trimethylamine.

Solvent.	*a*.	*b*.	Limit *k*.	Mean *k*.
Ethyl acetate ...	0·1647	0·1994	0·00650—0·00705	0·0067
Acetone	0·1362	0·1101	0·0680 —0·0700	0·069
Benzene	0·3006	0·3465	0·00247—0·00250	0·00248
Ethyl benzoate ...	0·2165	0·1497	0·0237 —0·0254	0·0238
Anisole	0·1894	0·2012	0·0205 —0·0217	0·0212
Nitrobenzene	0·0836	0·0492	0·211 —0·221	0·218

o-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1392	0·1699	0·00440—0·0046	0·00452
Acetone	0·0651	0·0730	0·0388 —0·0398	0·0394
Benzene	0·1855	0·1642	0·00155—0·00163	0·00160
Ethyl benzoate ...	0·0855	0·1248	0·0133 —0·0147	0·0139
Anisole	0·2365	0·1712	0·0111 —0·0113	0·0112
Nitrobenzene	0·1153	0·0711	0·0995 —0·103	0·101
Ethyl alcohol ...	0·1552	0·0835	0·0118 —0·0124	0·0122
94·45% Alcohol	0·1330	0·0726	0·0142 —0·0149	0·0145
Acetonitrile	0·1357	0·0771	0·129 —0·132	0·130

m-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1572	0·1339	0·0083 —0·0087	0·0085
Acetone	0·1334	0·0635	0·0541 —0·0578	0·0568
Benzene	0·1828	0·1538	0·00167—0·00190	0·0018
Ethyl benzoate ...	0·1961	0·1344	0·0155 —0·0164	0·0160
Anisole	0·2393	0·1904	0·0111 —0·0119	0·0114
Nitrobenzene	0·1182	0·0722	0·098 —0·103	0·102
Ethyl alcohol ...	0·1798	0·0909	0·0148 —0·0157	0·0151
94·45% Alcohol	0·1330	0·0722	0·0177 —0·0184	0·0179
Acetonitrile	0·0938	0·0449	0·141 —0·146	0·143

p-Nitrobenzyl chloride and trimethylamine.

Ethyl acetate ...	0·1572	0·1413	0·0104 —0·0113	0·0108
Acetone	0·1365	0·0627	0·0698 —0·0729	0·071
Benzene	0·1784	0·1604	0·00236—0·00250	0·0024
Ethyl benzoate ...	0·2062	0·1353	0·0214 —0·0227	0·0221
Anisole	0·2369	0·1847	0·0156 —0·0168	0·0160
Nitrobenzene	0·1167	0·0631	0·145 —0·157	0·150
Ethyl alcohol ...	0·1801	0·0881	0·0170 —0·0179	0·0175
94·45% Alcohol	0·1330	0·0695	0·0209 —0·0213	0·0210
Acetonitrile	0·0795	0·0437	0·158 —0·172	0·175

TABLE VIII.

Solubilities of the nitrobenzyl chlorides at 30°.

(G. of chloride per 100 g. of solvent.)

Solvent.	*ortho*-.	*meta*-.	*para*-.
Acetone	433	644	126·8
Benzene	304	—	74·2
Ethyl acetate	257	394	69·7
Nitrobenzene	217	326	68·2
Ethyl benzoate	171·3	266	51·2
Ethyl alcohol	26·3	30·4	8·2

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