422. *Velocities of Reaction of Substituted Benzyl Chlorides in Two Reactions of Opposed Polar Types.*

By G. M. BENNETT and BRYNMOR JONES.

THE contrasted modes of variation of velocities of reaction of substituted benzyl bromides were first pointed out and studied by Lapworth and Shoesmith (J., 1922, **121**, 1391, and subsequently), and in particular a study of the halogenated benzyl bromides was made by Shoesmith and Slater (J., 1926, 214). The fundamental principle involved was thus clearly established with reference to the two reactions chosen, *viz.*, hydrolysis (in presence of sodium hydroxide in the first paper, but subsequently acid hydrolysis in aqueous alcohol) and reduction with hydrogen iodide, but the results were in the form of comparative tests rather than accurate measurements of velocities of reaction. The reactions in question are not entirely satisfactory: the alkaline hydrolysis of benzyl chlorides is not a simple reaction (Olivier and Weber, *Rec. trav. chim.*, 1934, **53**, 869, 891); acid hydrolysis in alcoholic solution is known to involve simultaneous alcoholysis; and the reaction with hydrogen iodide is not convenient for accurate measurement.

It has been shown (Bennett and Berry, J., 1927, 1676; Baddeley and Bennett, J., 1933, 261) that two suitable reactions are acid hydrolysis in aqueous acetone solution and the reaction with potassium iodide in acetone solution studied by Conant and others (*J. Amer. Chem. Soc.*, 1924, **46**, 235; 1925, **47**, 448). In the present investigation we have applied these two reactions to a set of substituted benzyl chlorides (the velocity of reaction of the benzyl *bromides* with iodide is inconveniently high) with special attention to a complete series of halogeno-derivatives. The comparative velocities of hydrolysis in aqueous alcohol had been examined by Olivier, but the fluorobenzyl chlorides were not included in his series. Conant and his colleagues included the *o*- and *p*-chloro- and bromo-benzyl chlorides in their study of the reaction with iodide but other halogenated benzyl chlorides were not examined; moreover, the enormous difference in reaction velocity there found between the *p*-chloro- and *p*-bromo-benzyl chlorides seemed so improbable from the theoretical point of view as to call for reinvestigation, notwithstanding the fact that these authors had themselves realised this and had given the point special attention at the time. These figures have, moreover, been recently quoted again (Wilson, *Chem. Reviews*, 1935,

16, 183). The special importance of the halogens, and in particular of fluorine, arose in connexion with the discussion of the manner in which the halogens influence aromatic reactions (Bennett, J., 1933, 1112; Robinson, *ibid.*, p. 1114).

The measurements have now been made with benzyl chloride, its *p*-methyl and *o*-, *m*-, and *p*-nitro-derivatives, and the complete set of twelve halogeno-derivatives. Values of the activation energies have also been obtained to the degree of approximation given by measurements at two temperatures only.

The substances were prepared wherever possible from a purified solid intermediate. In particular, the *m*- and *p*-fluorobenzyl chlorides were each made from the corresponding fluorobenzyl alcohol regenerated from its pure *p*-nitrobenzoate, for some nuclear chlorination seemed unavoidable in the action of chlorine upon boiling *m*- and *p*-fluorotoluenes.

Conant's anomalous figures are now explained, since we have found that *p*-bromobenzyl chloride purchased from two different sources or made by chlorination of *p*-bromotoluene contains large amounts of *p*-chlorobenzyl bromide, and benzyl bromides react with iodide much faster than the chlorides. The displacement of nuclear bromine by chlorine was by no means surprising, but it seemed probable that bromine would thereby be completely lost with the production of *p*-chlorobenzyl chloride. A product actually obtained giving analytical figures close to those anticipated for the bromobenzyl chloride was consequently at first thought to be the authentic substance, but a synthesis of the chloride from *p*-bromobenzyl bromide through the pure alcohol showed that it was not so, and it is clear that, in spite of the presence of a rapid stream of chlorine, the bromine displaced from the nucleus of *p*-bromotoluene enters the side chain to a large extent in preference to chlorine, the actual reagent being presumably bromine chloride.

A similar observation was made in the *o*-series, and the pure *o*-bromobenzyl chloride must be prepared from pure *o*-bromobenzyl alcohol. The influence of these impurities on the velocity of reaction is enormous and suffices to account for the observations recorded by Conant, Kirner, and Hussey (*J. Amer. Chem. Soc.*, 1925, **47**, 488), where the reaction velocities for *o*- and *p*-bromobenzyl chlorides were found to be approximately 100 times those of the corresponding chlorobenzyl chlorides. One of our own specimens of *p*-bromobenzyl chloride containing the chlorobenzyl bromide gave constant velocity coefficients and a mean $k = 142$ as compared with the value $k = 3{\cdot}12$ found with the pure substance.

In Table I the figures for the velocities of hydrolysis at 69·8° and 84·5° and the activation energies for this reaction are given. The values of E vary but slightly from the mean figure 20,900 cals., and the differences from this value do not appear to be systematic. In one case, *viz.*, that of the *p*-chlorobenzyl chloride, a determination at 100·1° was made and the value $k = 0{\cdot}440$ found. The value of E calculated between 84·5° and 100·1° is 20,300 cals., identical with that found between 69·8° and 84·5°.

TABLE I.

Velocity Coefficients and Activation Energies for the Hydrolysis of Substituted Benzyl Chlorides in 50% Aqueous Acetone.

	Sub-stituent.	$k_{69\cdot8^\circ}$.	$k_{84\cdot5^\circ}$.	E, kg.-cals.	Variation of E from mean.		Sub-stituent.	$k_{69\cdot8^\circ}$.	$k_{84\cdot5^\circ}$.	E, kg.-cals.	Variation of E from mean.
	p-NO$_2$	0·00706	0·0246	20·6	−0·3	*p*	I	0·0296	0·1065	21·2	+0·3
	m-NO$_2$	0·00782	0·0285	21·3	+0·4		Br	0·0310	0·1158	21·7	+0·8
m	I	0·0143	0·0502	20·7	−0·2		Cl	0·0394	0·1330	20·3	−0·6
	Br	0·0132	0·0492	21·7	+0·8		F	0·1140	0·3820	20·0	−0·9
	Cl	0·0156	0·0556	21·0	+0·1		(H)	0·0671	0·2320	20·5	−0·4
	F	0·0159	0·0551	20·6	−0·3		*p*-CH$_3$	0·614	(and 0·1487 at 54·8°)	21·1	+0·2
o	I	0·0170	0·0605	21·0	+0·1						
	Br	0·0170	0·0642	22·0	+0·9						
	Cl	0·0194	0·0688	20·9	±0·0						
	F	0·0276	0·0995	21·2	+0·3						

The observed velocities of hydrolysis of halogeno-benzyl chlorides are approximately constant for the *m*-isomerides, but fall definitely in the *o*- and *p*-substances in the order

F$\gg$Cl$>$Br$>$I. The *p*/*m* velocity ratios which should be an indication of the electromeric effects are :

At 84·5°	F 6·94	Cl 2·39	Br 2·35	I 2·12
At 69·8°	7·17	2·53	2·35	2·07

Table II gives a comparison of the results for this reaction with those of Olivier : the agreement between the observations in the different solvents is generally good.

TABLE II.

Comparative Velocities of Hydrolysis of Halogenated Benzyl Chlorides.

(Benzyl chloride = 1·00.)

Substituent.	In 50% acetone at 84·5°.*	In 50% alcohol at 83°.†	Substituent.	In 50% acetone at 84·5°.*	In 50% alcohol at 83°.†
(H)	1·00	1·00	Br *o*-	0·277	0·286
F *o*-	0·429	—	*m*-	0·212	0·215
m-	0·238	—	*p*-	0·499	0·50
p-	1·65	—	I *o*-	0·261	0·287
Cl *o*-	0·296	0·355	*m*-	0·216	0·201
m-	0·240	0·237	*p*-	0·459	0·477
p-	0·573	0·62			

* This paper. † Olivier, *Rec. trav. chim.*, 1922, **41**, 646; 1923, **42**, 516, 775.

In Table III the corresponding figures for the reaction with potassium iodide in acetone solution are given. The values of *E* for this reaction again show little variation : it is, however, observable that the mean value of *E* for *o*-substituents is 17,300 cals., as compared with the mean for *m*-substituents of 18,100, and of *p*-substituents of 18,100. No systematic variation is apparent in the values for the various halogens in either *o*-, *m*-, or *p*-series. The mean values of the *m*/*p* velocity ratio are : F 0·93; Cl 0·79; Br 0·83; I 0·80.

TABLE III.

Velocity Coefficients and Activation Energies for the Reaction of Substituted Benzyl Chlorides with Potassium Iodide.

Substituent.	$k_{0\cdot1^\circ}$.	k_{20°.	*E*, kg.-cals.	Substituent.	$k_{0\cdot1^\circ}$.	k_{20°.	*E*, kg.-cals.
(H)	0·133	1·32	18·3	*o* F	0·450	3·89	17·2
m F	0·183	1·84	18·4	Cl	0·632	5·25	16·9
Cl	0·235	2·17	17·7	Br	0·565	5·27	17·8
Br	0·260	2·47	18·0	I	0·627	5·51	17·4
I	0·242	2·34	18·1	*m*-NO_2	0·486	4·83	18·4
p F	0·205	1·90	17·8	*p*-NO_2	0·907	8·17	17·6
Cl	0·293	2·80	18·0	*o*-NO_2	1·30	11·40	17·4
Br	0·301	3·12	18·7				
I	0·295	2·98	18·4				

The general opposed directions of variation of reaction velocity in the series for the two reactions are clear from Tables I and II which have been arranged to emphasise this point.

The particular significance of the arrangement of the halogens in the group is discussed in a subsequent paper.

EXPERIMENTAL.

Materials.—The benzyl chlorides were prepared either from the pure alcohol by the action of an excess of thionyl chloride and pyridine or by direct chlorination of the corresponding toluene. The requisite halogenated benzyl alcohols were obtained from the respective bromides or chlorides by heating with potassium carbonate in 50% acetone at the b. p. for 48—60 hours.

Benzyl chloride, from the halogen-free alcohol, had b. p. 66—67°/16 mm. (Found : C, 66·5; H, 5·6. Calc. : C, 66·4; H, 5·6%).

o-*Fluorobenzyl chloride* was prepared by chlorination of *o*-fluorotoluene from pure *o*-acetotoluidide. The portion of b. p. 170—185° was twice fractionated in a vacuum with a special glass column, affording a colourless liquid closely resembling the parent substance; b. p. 67·5—68°/16 mm. (Found : C, 57·6; H, 4·1; side-chain Cl, 24·7. C_7H_6ClF requires C, 58·1; H, 4·2; side-chain Cl, 24·5%).

The m-*isomeride* was prepared similarly from *m*-toluidine; the crude product was hydrolysed by continuous boiling for 1 week in 50% acetone, and the *m*-fluorobenzyl alcohol of b. p. 201° (uncorr.) converted into its p-*nitrobenzoate*, which, from ethyl acetate and ligroin, forms monoclinic plates with an oblique extinction, m. p. 86° (Found: C, 61·1; H, 3·8. $C_{14}H_{10}O_4NF$ requires C, 61·1; H, 3·7%). The regenerated alcohol yielded the pure *m*-fluorobenzyl chloride as a colourless liquid, of b. p. 67—68°/15 mm. (Found: C, 57·9; H, 4·2%).

p-*Fluorobenzyl chloride*, prepared from toluidine, formed a similar colourless liquid of b. p. 69—70°/15 mm. (Found: C, 58·3; H, 4·2%). In order to ensure purity, the chloride was hydrolysed, and the fluorobenzyl alcohol isolated and converted into its p-*nitrobenzoate*, which, from ethyl acetate–ligroin (b. p. 60—80°), formed small, almost colourless, pointed needles with straight extinction, m. p. 98° (Found: C, 61·3; H, 3·8%). This ester was hydrolysed, and the recovered alcohol converted into the pure chloride, b. p. 76°/20 mm. (Found: C, 58·0; H, 4·3%).

o-Chlorobenzyl chloride, from the pure alcohol, had b. p. 94°/15 mm. (Found: C, 52·2; H, 3·8. Calc.: C, 52·2; H, 3·8%). The *m*-isomeride, by chlorination of *m*-chlorotoluene, had b. p. 104°/17 mm. (Found: C, 52·15; H, 3·6; Cl, 43·9; side-chain Cl, 22·5. Calc.: Cl, 44·0; side-chain, 22·0%); and the *p*-isomeride, recrystallised from light petroleum and acetic acid, had m. p. 29° (Found: C, 52·4; H, 3·8%).

o-*Bromobenzyl chloride*. A purchased specimen on hydrolysis yielded *o*-chlorobenzyl alcohol and was therefore rejected. Our specimen from the pure bromo-alcohol had b. p. 105—106°/12 mm. (Found: C, 41·2; H, 3·0. Calc.: C, 40·9; H, 2·9%). The *m*-bromo-compound, from the pure alcohol of b. p. 138°/15 mm., was a colourless lachrymatory liquid of b. p. 111—112°/15 mm. (Found: C, 40·9; H, 2·8%).

p-*Bromobenzyl chloride*. (a) A purchased specimen, twice recrystallised from light petroleum, had m. p. 45·5° (Found: C, 37·9; H, 2·8; Cl + Br, 58·5. Calc.: C, 40·9; H, 2·9; Cl + Br, 56·2%). (b) The product of chlorination from *p*-bromotoluene solidified after distillation and was similarly recrystallised; it had m. p. 45° (Found: C, 40·1; H, 2·7; Cl + Br, 56·5%). After this had been twice recrystallised from glacial acetic acid (in which it is readily soluble) the substance gave a velocity coefficient of reaction with potassium iodide at 20° of 142, whereas the true value is 3·12. (c) The substance was obtained pure *via* the purified bromo-alcohol from *p*-bromobenzyl bromide. It was distilled at 137°/37 mm. and had m. p. 36° (Found: C, 40·7; H, 2·9%).

o-Iodobenzyl chloride, obtained from the alcohol of m. p. 87° (Found: C, 36·3; H, 3·0. Calc.: C, 35·9; H, 3·0%), distilled at 147—149°/32 mm. and had m. p. 27° (Found: C, 33·6; H, 2·5. Calc.: C, 33·3; H, 2·4%). The *m*-isomeride was prepared from the corresponding bromide of m. p. 49° (Found: C, 28·4; H, 2·05. Calc.: C, 28·3; H, 2·0%) through the alcohol of b. p. 151—155°/13 mm., as a colourless lachrymatory liquid of b. p. 134—136°/14 mm. (Found: C, 33·2; H, 2·35%).

p-Iodobenzyl chloride, from the alcohol, formed a colourless solid of m. p. 53° after three crystallisations from light petroleum (Found: C, 33·5; H, 2·3; side-chain Cl, 14·1. Calc.: side-chain Cl, 14·0%). In one preparation recrystallisation showed the presence of a substance of higher m. p., 108°, which formed nearly colourless, highly refractive, monoclinic plates slightly soluble in ligroin. This contains sulphur and is *di*-p-*iodobenzyl sulphite* (Found: C, 32·8; H, 2·3; I, 49·2. $C_{14}H_{12}O_3SI_2$ requires C, 32·7; H, 2·3; I, 49·4%).

p-Methylbenzyl chloride was obtained by chlorination of *p*-xylene, the fraction of b. p. 180—205° being distilled in a vacuum. It was a colourless liquid of b. p. 81°/15 mm. (Found: C, 68·2; H, 6·3; side-chain Cl, 24·4. Calc.: C, 68·4; H, 6·5; side-chain Cl, 25·2%). The weights of this substance used were corrected for the small proportion (3·3%) of inert chlorotoluene present [compare Olivier (*Rec. trav. chim.*, 1922, **41**, 649), whose product by this method was largely nuclear-chlorinated material].

The *o*-, *m*-, and *p*-nitrobenzyl chlorides were each twice recrystallised from acetic acid and melted at 49·5°, 45·5°, and 72·5° respectively.

Velocity Measurements.—The velocity of hydrolysis was measured by the methods previously described (Baddeley and Bennett, *loc. cit.*), the materials for each reading being separately sealed up in glass tubes. The technique in the measurements of the velocity of reaction with iodide was also as before, except that the lower temperature of working permitted the use of a stoppered flask for the reaction and the removal of aliquot portions with a pipette. Complete details for two substances in the first reaction are shown in Table IV and for three substances in the second reaction in Table V. *o*-Nitrobenzyl chloride is omitted from the series of observed velocities of hydrolysis since the solutions darkened and the reaction must be complicated by some subsidiary reaction.

TABLE IV.

Hydrolysis of substituted benzyl chlorides in 50% *acetone.*

p-Iodobenzyl chloride at 84·5°.

Time (hrs.)	0	1·733	2·233	3·150	3·750	4·483	5·083	8·00	
Titre, c.c.	0·27	1·66	2·06	2·69	3·10	3·50	3·85	5·17	
$(a - x)$, c.c.	8·50	7·11	6·71	6·08	5·67	5·27	4·92	3·60	
k	—	0·103	0·106	0·106	0·108	0·107	0·108	0·107	Mean 0·1065

m-Bromobenzyl chloride at 69·8°.

Time (hrs.)	0	4·067	6·167	10·00	22·88	25·62	32·42	
Titre, c.c.	0·16	0·60	0·84	1·24	2·42	2·63	3·11	
$(a - x)$, c.c.	8·61	8·17	7·93	7·53	6·35	6·14	5·66	
k	—	0·0129	0·0133	0·0134	0·0133	0·0132	0·0129	Mean 0·0132

TABLE V.

Reaction of substituted benzyl chlorides with potassium iodide in acetone.

(Titres, A, represent c.c. of 0·003M-KIO_3.)

o-Fluorobenzyl chloride at 20°.

Time $(t_2 - t_1)$, hrs.	—	0	0·1186	0·2814	0·4214	0·5659	0·7550	
Titre, A	33·33 (A_0)	31·26 (A_1)	28·53	25·34	22·76	20·74	17·70	
k	—	—	3·928	3·846	3·911	3·797	3·987	Mean 3·894

p-Bromobenzyl chloride at 20°.

Time $(t_2 - t_1)$, hrs.	—	0	0·1261	0·2525	0·3936	0·6087	0·8637	
Titre, A	33·33 (A_0)	30·24 (A_1)	28·02	25·74	23·77	21·04	18·11	
k	—	—	3·096	3·131	3·182	3·129	3·147	Mean 3·137

An independent experiment gave mean k = 3·108.

p-Nitrobenzyl chloride at 0·1°.

Time $(t_2 - t_1)$, hrs.	—	0	0·247	0·508	0·810	1·183	1·357	2·654
Titre, A	33·33 (A_0)	32·06 (A_1)	30·67	29·25	27·78	26·00	25·19	20·21
k	—	—	0·8976	0·9154	0·8995	0·9067	0·9145	0·9103
								Mean 0·907

For the reaction with iodide, the molecular ratio used was in general organic halide : KI = 5·13 : 1. The closeness of agreement in duplicate experiments is shown by the values in independent runs, *viz.*, for *o*-nitrobenzyl chloride at 20·0°, 11·24 and 11·55; for *p*-bromobenzyl chloride at 20·0°, 3·137 and 3·108. The extent of variation of the velocity coefficient with molecular proportions of organic halide to iodide is shown by the following mean values at 20·0°.

p-$Cl{\cdot}C_6H_4{\cdot}CH_2Cl$: KI =	5·13 : 1	2 : 1	8 : 1
k	2·80	2·66	2·83

o-$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl$: KI =	5·1 : 1	2 : 1
k	11·40	11·18

The authors thank Mr. J. H. Higham for valuable assistance in the preparation of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, September* 30*th*, 1935.]