118. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part III. The Effect of Unipolar Substituents on the Critical Energy and Probability Factors in the Interaction of Benzyl Bromide with Pyridine and α-Picoline in Various Solvents.*

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EARLIER results (Baker, J., 1934, 987; cf. J., 1933, 1128), derived from preliminary kinetic studies of the interaction of benzyl bromides with pyridine, indicated the necessity for a detailed kinetic analysis of this reaction, especially in relation to the effects of various factors upon its critical energy. Accurate data are now recorded for the energy of activation of the reaction between substituted benzyl bromides with pyridine and α-picoline in dry and in aqueous acetone and in aqueous alcohol, and the effects of both the base and the solvent on the various terms in the modified Arrhenius equation $k_p = PZ \, . \, e^{-E/RT}$ are analysed. For reasons previously discussed (*loc. cit.*), the investigation is restricted, at present, to substituents of a unipolar ($\pm I$) type.

In Part II (*loc. cit.*) it was shown that the velocity of interaction of benzyl halides and dry acetone (solvent reaction) was small (1—2%) in comparison with that of their reaction with pyridine. Improved methods of purification of materials have now reduced the velocity of such solvent reactions (k_s* $= 7 \times 10^{-8}$ sec.$^{-1}$) to approximately 0·5% of that of the main reaction, and this can be ignored as being well within the probable experimental error (1—2%).

The essential bimolecular nature of the reaction, previously established for benzyl bromide (Part II), was first confirmed in the case of the *p*-nitro-derivative by variation in the concentration of both reactants. The data are summarised in Table I (time throughout is in seconds). A slight upward drift in the value of k_p is again observed in the presence of a *large* excess of the bromide. This drift is probably explained by the superimposition of the small solvent reaction, which becomes relatively more important when the concentration of the pyridine is very small, and the rather larger experimental error involved in measurements at such dilution. Moreover, determination of the uncombined pyridine (Table II) by the method described on p. 525 shows clearly that throughout the reaction the free base disappears at the same rate as that at which the bromide ion is formed. The reaction is thus of the first order with respect to each reactant.

TABLE I.

Effect of concentration on the velocity of interaction of *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2Br$ (c_a) and pyridine (c_p), in dry acetone at 40°.

c_a.	c_p.	c_a/c_p.	$k_p \times 10^4$.	c_a.	c_p.	c_a/c_p.	$k_p \times 10^4$.
0·0125	0·0125	1	4·217	0·0250	0·0125	2·0	4·417
0·0050	0·0125	0·4	4·467	0·0250	0·0025	10·0	4·833

TABLE II.

Interaction of CH_2PhBr with pyridine, both 0·025*M*, in dry acetone at 30° (20-c.c. samples).

Time, mins.	0	10	1040	1400	2590
C.c. of *N*/20-NH_4SCN equiv. to unchanged CH_2PhBr	(10)	9·94	7·27	6·48	5·12
C.c. of *N*/20-H_2SO_4 equiv. to free C_5H_5N	(10)	9·94	7·26	6·42	5·19

In Part II, the catalytic influence of added salts was suggested, but more detailed investigations have revealed the existence of a definite equilibrium

$$\mathrm{ArBr} + \mathrm{ArC_5H_5}\overset{\oplus}{\mathrm{N}}\}\overset{\ominus}{\mathrm{N}}\mathrm{O_3} \rightleftharpoons \mathrm{ArO{\cdot}NO_2} + \mathrm{ArC_5H_5}\overset{\oplus}{\mathrm{N}}\}\overset{\ominus}{\mathrm{Br}}$$

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* As in Part II, k_s = the pseudo-unimolecular velocity coefficient for the solvent reaction, k_p = the *true* bimolecular velocity coefficient for the reaction with the cyclic base; c_a, c_p, and c_s are, respectively, the concentrations of aryl halide, cyclic base, and salt, in g.-mol. per litre.

which is established with a measurable velocity. The kinetics of this reversible reaction are under investigation, but meanwhile it must be noted that such interaction of the foreign anion with the benzyl bromide vitiates the use of the standard conditions of comparison ($c_a = c_p = c_s = 0{\cdot}025$ g.-mol./l) previously employed. The quaternary bromide formed exerts a definite, although small, catalytic influence upon the reaction between benzyl bromide and pyridine in dry acetone. The data are in Table III.

TABLE III.

Effect of benzylpyridinium bromide (*s*) on the velocity of interaction of benzyl bromide with pyridine in dry acetone at 30° ($c_a = c_p = 0{\cdot}025$).

c_s	0	0·0129	0·0259
Bimol. $k \times 10^4$ (sec.$^{-1}$)	2·430	2·550	2·613
Mean deviation from mean $\times 10^4$	0·012	0·023	0·033

The slight upward drift observed in the bimolecular coefficient after about 40% reaction is explained by this effect superimposed upon the small solvent reaction which has been neglected. Such acceleration is negligible within the first 30—40% of the reaction. Hence the standard conditions employed throughout this paper are $c_a = c_p = 0{\cdot}025M$, without added salt, velocity measurements being restricted to the first 20—30% of the reaction.

The data obtained under such standard conditions for the reaction between various benzyl bromides with pyridine or α-picoline in dry and aqueous 90% acetone and in 90% alcohol (both by wt.) at various temperatures are summarised in Table IV. The k_p values (in g.-mol./l./sec.) have been determined from the slope of the straight line obtained by plotting $x/(a-x)$ against time, and, in the case of 90% alcohol, are corrected for the solvent reaction as described in Part II.* Within the limits of experimental error, the plot of $\log_e k$ against $1/T_{\text{abs.}}$ in all cases gives a straight line, from the slope of which the value of E has been determined. The values of Z are the theoretical collision values (at 30°) obtained from the relationship $5{\cdot}71 \times 10^{25} . T^{\frac{1}{2}}[(M_1 + M_2)/M_1M_2]^{\frac{1}{2}}[(\sigma_1 + \sigma_2)/2]^2$ (Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241), molecular diameters being computed on the basis of parachor values (Nathan and Watson, J., 1933, 890). Substitution of α-picoline for pyridine makes a difference of only one unit in the third decimal place of $Z \times 10^{-11}$, so no appreciable error is introduced by using the same values throughout. The recorded mean values of P (the probability factor) are those derived from the modified Arrhenius equation $k_p = PZ . e^{-E/RT}$, whence the calculated values of k_p (col. 6) are derived.

Discussion.—Any discussion of the data summarised above falls naturally into two sections, *viz.*, (A) conclusions which seem to be fairly definitely established by the experimental results, and (B) tentative suggestions which may partly explain some of the more complicated phenomena and also indicate further lines of investigation with a view to testing their validity.

(A) It has already been suggested (Part II) that it is not possible to separate the energy requirements of the two processes (of opposite polar requirements) involved in the formation of the quaternary bromide, *viz.*, (1) the anionisation of the bromine, and (2) the electrostriction and co-ordination of the base to the carbon. This conclusion would seem to be definitely established by the observation that the activation energies for the reaction of all three benzyl bromides with pyridine are almost identical with the corresponding values in the interaction with α-picoline, in spite of the fact that the basic strength of the latter ($K_b = 3 \times 10^{-8}$) is ten times as great as that of the former ($K_b = 2{\cdot}3 \times 10^{-9}$), a factor which must greatly facilitate process (2). Moreover, in each series, the activation energies of the *p*-methyl- and *p*-nitro-derivatives differ but slightly from that of the unsubstituted parent. Such observations, coupled with the bimolecular character of the reaction, clearly indicate that, in non-ionising solvents, the reaction mechanism is

* The solvent reaction in 90% acetone is of the same order ($k_s = 7 \times 10^{-8}$ sec.$^{-1}$ with benzyl bromide) as that in dry acetone, and is still within the limits of the experimental error.

TABLE IV.

Kinetic data for the interaction of p-$C_6H_4R{\cdot}CH_2Br$ with pyridine (Py.) and α-picoline (Pic.) in various solvents ($c_a = c_p = 0{\cdot}025M$).

No.	Base.	R.	Temp.*	$k_p \times 10^4$. Found.	$k_p \times 10^4$. Calc.†	E, cals.	$P \times 10^6$.	$Z \times 10^{-11}$ (at 30°).
I. *In dry acetone.*								
1	Py.	H	0°	0·248	0·247	12,460	0·870	2·776
2	,,	H	20	1·223	1·236			
3	,,	H	30	2·450	2·496			
4	,,	H	40	4·817	4·818			
5	,,	Me	0	$0{\cdot}420_5$	0·426	11,900	0·515	2·866
6	,,	Me	20	2·020	1·980			
7	,,	Me	30	3·900	3·887			
8	,,	Me	40	7·150	7·250			
9	,,	NO_2	0	0·231	0·231	12,310	0·607	2·816
10	,,	NO_2	20	1·122	1·132			
11	,,	NO_2	30	2·267	2·269			
12	,,	NO_2	40	4·333	4·344			
13	Pic.	H	20	0·183	0·181	12,480	0·132	2·776
14	,,	H	30	0·367	0·365			
15	,,	H	40	0·705	0·701			
16	,,	Me	20	0·328	0·326	12,190	0·139	2·866
17	,,	Me	30	0·647	0·648			
18	,,	Me	40	1·240	1·232			
19	,,	NO_2	20	0·127	0·126	12,100	0·0470	2·816
20	,,	NO_2	30	0·248	0·249			
21	,,	NO_2	40	0·475	0·472			
II. *In aqueous* 90% *acetone.*								
22	Py.	H	20	2·342	2·345	13,710	13·97	2·776
23	,,	H	40	10·470	10·468			
24	,,	Me	20	4·200	4·200	13,680	23·17	2·866
25	,,	Me	40	18·700	18·622			
26	,,	NO_2	20	1·580	1·581	13,840	11·70	2·816
27	,,	NO_2	40	7·167	7·163			
III. *In aqueous* 90% *alcohol.*								
28	Py.	H	20	1·297	1·290	15,310	120·81	2·776
29	,,	H	30	3·075	3·095			
30	,,	Me	20	2·840	2·830	16,000	836·74	2·866
31	,,	Me	30	7·000	7·026			
32	,,	NO_2	20	0·422	0·419	15,810	91·377	2·816
33	,,	NO_2	30	1·029	1·036			

* Temperatures recorded as 0°, 20°, 30°, 40° are actually − 0·5°, 20·0°, 29·95°, and 39·9°, respectively, as determined by a calibrated N.P.L. standard thermometer.

† The relative values of k_p are probably accurate to 1—2%, although systematic errors essential to the technique probably make the *absolute* values subject to an error of 3—4%. The probable error in E values determined from velocity data at three or four temperatures (Section I) is of the order of 100 cals., but in those determined at only two temperatures (Sections II and III), a somewhat larger error may be anticipated, especially in Section III, where the correction for the solvent reaction is relatively large.

essentially one of simultaneous addition and dissociation of the type proposed by London (*Z. Elektrochem.*, 1929, **35**, 552) on quantum-mechanical grounds, and recently discussed by Hughes and Ingold (this vol., p. 244; mechanism S_N2) in their generalised theory of reaction at a saturated carbon atom : $C_5H_5\overset{\curvearrowright}{N}\ \overset{\curvearrowright}{Ar{-}Br} \longrightarrow C_5H_5\overset{\oplus}{N}Ar + \overset{\ominus}{Br}$. A precisely similar conclusion has been reached by Hammett and Pfluger (*J. Amer. Chem. Soc.*, 1933, **55**, 4079) in the case of the comparable reaction between trimethylamine and alkyl acetates.

Another interesting aspect of the results is revealed by the velocity ratios for the substituted and the unsubstituted benzyl bromides given in Table V, in which the ratios of the probability factors are also shown.

It has already been established (Part II) that the effect of unipolar substituents on velocity varies enormously from reaction to reaction, even although *all* such reactions

TABLE V.

The effect of the substituent R on the velocity of interaction of p-$C_6H_4R{\cdot}CH_2Br$ with pyridine and α-picoline in various solvents.

		Dry $COMe_2$.		90% $COMe_2$		90% EtOH.	
R.	Temp.	k_R/k_H.	P_R/P_H.	k_R/k_H.	P_R/P_H.	k_R/k_H.	P_R/P_H.
Pyridine.							
Me	0°	1·69	0·59	—	1·65	—	6·9
,,	20	1·66		1·79		2·19	
,,	30	1·59		—		2·28	
,,	40	1·48		1·79		—	
NO_2	0	0·93	0·70	—	0·84	—	0·76
,,	20	0·917		0·675		0·325	
,,	30	0·925		—		0·334	
,,	40	0·900		0·717		—	
α-Picoline in dry acetone.							
R=Me	$t=$ 0	1·84	1·05				
,,	20	1·76					
,,	30	1·76					
R=NO_2	$t=$ 0	0·696	0·35				
,,	20	0·663					
,,	30	0·674					

involve attack by nucleophilic reagents and anionisation of the halogen in the formation of the ultimate product. The results in Table V now clearly indicate that the effect of such substituent groups upon the velocity of one particular reaction is largely dependent upon the nature of the medium,* and, to a smaller extent, upon that of the base. This is especially noticeable in the case of a *p*-nitro-substituent, a group which has always been considered to exert a strong retarding influence upon reactions which require electron accession to the side chain. Such retarding influence is clearly marked in 90% alcohol but is almost non-existent in dry acetone, the velocity of the *p*-nitro-compound in this medium being 90—95% of that of the unsubstituted parent. In the face of such results, it seems difficult any longer to assume, at least in the example of quaternary-salt formation in non-ionising media under consideration, that the general inductive polar effect of substituents is concerned mainly with the degree of polarisation or with the polarisability of the carbon–halogen bond. This differentiation in the effects of unipolar substituents upon velocity leads us naturally into a more detailed consideration of the effect of solvent upon the various factors in the reaction.

(B) Examination of the data in Table IV leads to the following clearly defined experimental conclusions, quite independently of any theoretical interpretation. Consideration being restricted first to the reaction with pyridine, it is apparent that in the solvent series dry acetone (Nos. 1—12), aqueous acetone (Nos. 22—27), and aqueous alcohol (Nos. 28—33), *i.e.*, in a series representing increasing ionising power, the continual increase in velocity is accompanied by a parallel *increase* (1) in the energy of activation (12,000 to 16,000 cals.), and (2) in the magnitude of the retarding or accelerating effect of the *p*-substituent group, *i.e.*, in the relative separation of the velocities of the unsubstituted and the substituted benzyl bromides. In any one solvent, the activation energies of the three benzyl bromides are almost identical, the differentiation in their velocities being accounted for almost entirely by the different values of the probability factor. These P factors, which are small and essentially the same for all three derivatives in dry acetone, become increasingly larger and also increasingly divergent in aqueous acetone and in aqueous alcohol (cf. Table V). In this connexion, it is of interest that Hughes (this vol., p. 255) found that the E value for the unimolecular ionisation of chlorine from carbon, in the case of *tert.*-butyl chloride in aqueous 80% acetone, is of much higher order, *viz.*, 22,600 cals. This value is closely similar to those which we have observed (Table VI) for the (probably pseudo-unimolecular) reaction between the aryl halides and aqueous 90% alcohol (the solvent reaction). Such data suggest that, in aqueous solvents, the reaction mechanism of quaternary-salt formation may approach

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* A similar result was established by McCombie, Scarborough, and Smith (J., 1927, 802) for the reaction between *o*-, *m*-, and *p*-nitrobenzyl chlorides with trimethylamine.

the type (whatever that may be *) involved in the hydrolysis reactions. The present results supply no evidence for the existence of a superimposed unimolecular reaction, $\mathrm{Ar{-}Br} \longrightarrow \overset{\oplus}{\mathrm{Ar}} + \overset{\ominus}{\mathrm{Br}}$; $\overset{\oplus}{\mathrm{Ar}} + \mathrm{C_5H_5N} \longrightarrow \mathrm{C_5H_5\overset{\oplus}{N}Ar}$, in dry acetone, but it has previously been suggested (Baker, J., 1932, 2631) that, in aqueous 90% alcohol, *p*-methoxybenzyl bromide *does* react by this mechanism, the initial ionisation in this case being rapid.

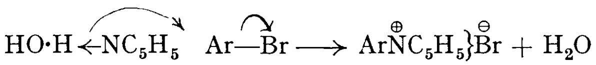
TABLE VI.

Action of aqueous 90% EtOH (by wt.) on p-$\mathrm{C_6H_4R{\cdot}CH_2Br}$.

R.	Temp.	Unimol. $k_s \times 10^6$, sec.$^{-1}$.	E (Arrhenius), cals.
H	20°	0·817	23,910
H	30	3·17	
Me	20	3·53	23,870
Me	30	12·0	
NO_2	20	0·125	22,870
NO_2	30	0·350	

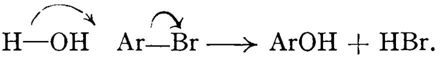
The conversion of a neutral pyridine molecule into the positively charged pyridinium cation, *e.g.*, in its reaction with an acid, is an exothermic reaction, and it is tentatively suggested that the similar conversion of pyridine into the benzylpyridinium cation, once the (probably low) energy barrier is surmounted, liberates energy which may be utilised in the concomitant ionisation of the bromine atom, thus accounting for the much lower energy of activation observed in the bimolecular reaction.

It is considered almost certain that in dry acetone the attacking reagent is a pyridine *molecule*, but in aqueous media the formation of pyridinium complexes, of varying degrees of electrostriction up to the limiting type $\mathrm{C_5H_5\overset{\oplus}{N}} \longrightarrow \overset{\ominus}{\mathrm{H}}\mathrm{{\cdot}OH}$, might be anticipated. The interaction of such complexes with the aryl halides to form the quaternary salt must involve the rupture of the co-ordinate link between the nitrogen atom and the water molecule :



$$\mathrm{HO{\cdot}H \leftarrow NC_5H_5 \quad Ar{-}Br \longrightarrow Ar\overset{\oplus}{N}C_5H_5\}\overset{\ominus}{Br} + H_2O}$$

and the additional energy requirements of this stage might account for the larger energy of activation observed in aqueous acetone and alcohol. On this view, the higher energy of activation required in the hydrolysis of the aryl bromide in aqueous alcohol (Table VI) could be regarded as arising from the necessary rupture of a normal covalent link between oxygen and hydrogen :



$$\mathrm{H{-}OH \quad Ar{-}Br \longrightarrow ArOH + HBr.}$$

The relatively greater effects of *p*-methyl (accelerating) and *p*-nitro (retarding) substituents in aqueous media could then be correlated with their effects in facilitating and preventing, respectively, the appropriate orientation of the attacking charged complex to the α-carbon. It is significant that, as already noted, the greater differentiation between the velocities of the *p*-methyl, *p*-hydrogen, and *p*-nitro-derivatives in aqueous media (Table IV, Sections II and III) depends mainly on the P and not on the E term in the modified Arrhenius equation. In reactions where the approach of a charged ion and not a neutral molecule is involved, the presence of the charge upon the attacking entity may, we think, introduce further complications, particularly with regard to the orientation and approximation of the attacking reagent to the seat of attack. Thus in attack by a negatively charged ion upon a saturated carbon atom, the ion must penetrate the surrounding electronic field of the atom, and this may well be an important factor in determining the critical increment of such reactions. It is anticipated that the critical-energy

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* The possibility of the formation of an intermediate complex, which may then decompose unimolecularly, $\mathrm{ArBr + C_5H_5N} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{complex} \xrightarrow{k_3} \mathrm{product}$, must be kept in mind. The reaction kinetics in such a case would then depend upon the relative magnitudes of k_1, k_2, and k_3.

increments and velocities of the forward and the reverse reaction in the salt equilibrium referred to on p. 519, which is essentially an attack by a negative ion, $\mathrm{ArBr} + \overset{\ominus}{\mathrm{NO_3}} \rightleftharpoons \mathrm{ArO{\cdot}NO_2} + \overset{\ominus}{\mathrm{Br}}$, will throw light on this aspect of the problem.

In conclusion, two other points must be briefly discussed. The first is the much slower reaction observed with the stronger base α-picoline (Nos. 13—21) than with the weaker base pyridine (Nos. 1—12) under otherwise identical conditions. It will be noticed (Table IV) that the E terms with both bases are practically identical, the velocity differentiation being accounted for entirely by the smaller value of the probability factor in the former case. We suggest that this is due largely to the steric effect of the α-methyl group, possibly accentuated by an orientation effect due to the more pronounced polar character of the picoline molecule.

The second point is the rather lower value for E observed in the reaction between *p*-methylbenzyl bromide and pyridine. The difference (500—600 cals.) is larger than the estimated experimental error in this series, and suggests the existence of a real, but small, facilitating effect of the *p*-methyl group. Further discussion of this point would be premature until the results of work now in hand are available, particularly that part of it dealing with the effects of an extended series of unipolar substituents in both the meta- and the para-position.

EXPERIMENTAL.

Purification of Materials.—*Acetone.* Since large volumes of pure acetone were required, the feasibility of employing A. R. acetone (B.D.H.) was explored, but it was found that, even after drying with calcium chloride and careful fractionation through a column, the sample still showed considerable reactivity with benzyl bromide. Such reactivity, moreover, was not removed by refluxing a solution of benzyl bromide and pyridine (both $0{\cdot}025M$) in the acetone for 5 days, to complete quaternary-salt formation, and recovering the solvent by careful fractionation. The only satisfactory material is that regenerated from the sodium iodide compound (supplied by B.D.H.). This was dried for several days over sodium sulphate, fractionated through a column, and the process repeated on the constant-boiling fraction. The sample thus obtained, b.p. 56·2°, was almost free from activity towards pure benzyl bromide (Found: $k_{\text{unimol.}} = 0{\cdot}71 \times 10^{-7}$ sec.$^{-1}$ in $0{\cdot}025M$-solution at 30°). The "heads" and "tails" from the fractionation were left in contact with a little solid potassium permanganate and sodium sulphate for 7 days, and again treated as above, a further quantity of suitable acetone being thus obtained. The aqueous acetone was prepared from this sample and distilled water by direct weighing. The aqueous alcohol was the sample used in Part II.

Benzyl bromides. Benzyl bromide was repeatedly fractionated under reduced pressure. The constant-boiling fraction was then gently refluxed, in the distillation apparatus, with a few drops of pure pyridine; the resulting hygroscopic quaternary salt removed any remaining traces of water. Refractionation gave a sample, b. p. 82°/11 mm., which was again distilled in a vacuum immediately prior to each velocity determination. The refractive index (not recorded in the literature) was $n_{\mathrm{D}}^{22^\circ}$ 1·5742. The *p*-methylbenzyl bromide was first purified by repeated crystallisation from ligroin (b. p. 40—60°), and the sample, m. p. 36·2°, was then distilled first with pyridine and finally alone, as in the case of benzyl bromide. *p*-Nitrobenzyl bromide was purified by repeated crystallisation, first from 95% alcohol and then from ligroin (b. p. 40—60°); m. p. 98·9°.

Pyridine. A "pure" commercial specimen (Monsanto) was dried over fused potassium hydroxide and repeatedly fractionated through a long pear-head column in an all-glass apparatus. The middle fraction was refluxed with a few c.c. of pure benzyl bromide, and again fractionated, only the middle fraction of constant b. p. 116·5° being employed.

α-Picoline. This was repeatedly fractionated, first under atmospheric pressure through a long column, and then repeatedly under reduced pressure until all low-(pyridine) and high-boiling fractions were eliminated. It was then treated with benzyl bromide, and the purification completed as for pyridine; b. p. 50·5—50·7°/38 mm.

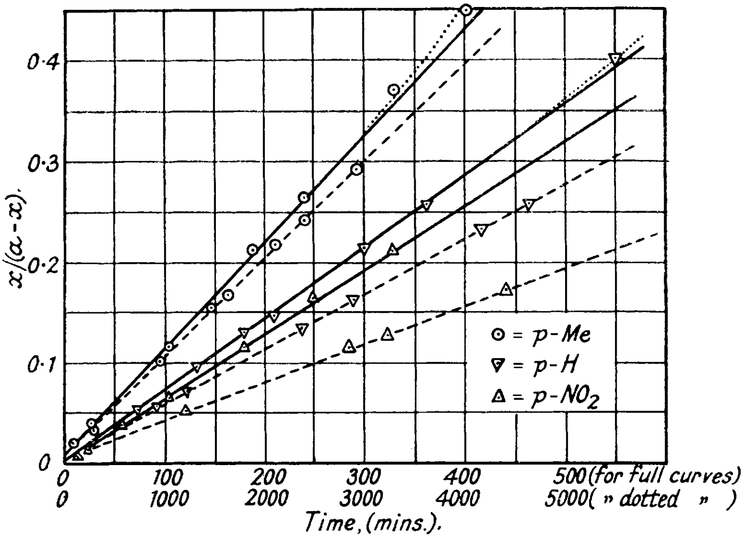
Velocity Determinations.—The technique was essentially that previously used (*loc. cit.*) except that there was a tendency for a small amount of benzyl and *p*-methylbenzyl bromides to remain in the initial aqueous–acetone layer. To avoid this, the following technique was finally adopted. The reaction sample (20 c.c.) was run into about 80 c.c. each of water and ether, and the quaternary salt washed out by repeated extractions with 10—20 c.c. portions of water. To the combined aqueous liquors, about 90% of the estimated volume of *N*/20-ammonium thiocyanate solution was added from a N.P.L. standard 10 c.c. burette, a few c.c. of pure nitric acid added, followed by 10 c.c. of *N*/20-silver nitrate (from a standard pipette). After addition of the ferric indicator, titration of the excess of silver nitrate was rapidly completed with the standard thiocyanate solution. In this manner, any minute trace of the aryl halide which might still have passed into the aqueous layer was only in contact with a very small concentration of silver nitrate for a short time, so that interaction between the two substances was negligible.

All samples were taken out at the temperature of the thermostat, pipettes being kept in suitable containers in the thermostat itself.

Since it was found unnecessary to stir the homogeneous reaction mixture, the velocity determinations were carried out in long-necked, stoppered, glass flasks instead of the more complicated apparatus previously employed.

Temperature control, by electrically operated thermo-regulators, was accurate to ± 0·02°, as recorded on Beckmann thermometers, actual temperatures being determined by a N.P.L. standard thermometer. Measurements at — 0·50° were conducted in a rapidly stirred mixture of crushed ice and water in a bath suitably insulated in a packed wooden box. The Beckmann thermometer was, in this case, calibrated against the N.P.L. standard thermometer at 0° in a bath of melting ice prepared from pure distilled water.

Fig. 1.



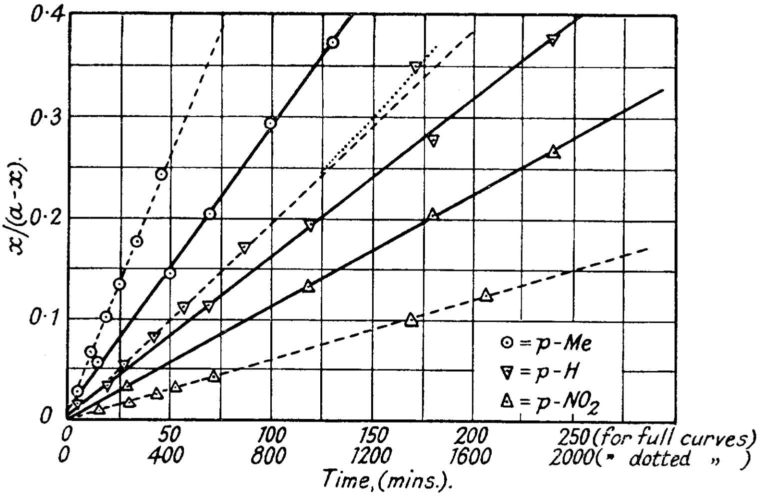
Full curves ——— = $C_6H_4R{\cdot}CH_2Br$ + *pyridine in dry acetone at* 40°.
Dotted curves – – – = $C_6H_4R{\cdot}CH_2Br$ + *α-picoline in dry acetone at* 30°.

Determination of Pyridine and α-Picoline.—In order to follow the reaction by observations of the rate of removal of the base, an empirical method for the rapid determination of very small concentrations of pyridine and α-picoline was developed. The reaction sample (20 c.c.) was pipetted into 5 c.c. of water and 30 c.c. of ether (to remove all the aryl bromide from the aqueous layer), and the base extracted with a known volume of *N*/20-sulphuric acid under standard conditions. The excess of acid in the aqueous layer was titrated with *N*/20-sodium carbonate and bromophenol-blue. The end point was taken at an intermediate green shade, which was matched against an artificial colour standard (an aqueous solution containing 0·075 g. of potassium dichromate and 1·5 g. of chrome alum per l.). The accuracy of the method (approx. 1%) was checked with known amounts of the two bases over the whole concentration range required.

	Pyridine, mg.					α-Picoline, mg.		
Taken	7·87	15·73	23·60	31·47	39·47	18·61	32·57	46·53
Found	8·10	15·68	23·55	31·32	39·14	18·46	32·42	46·45

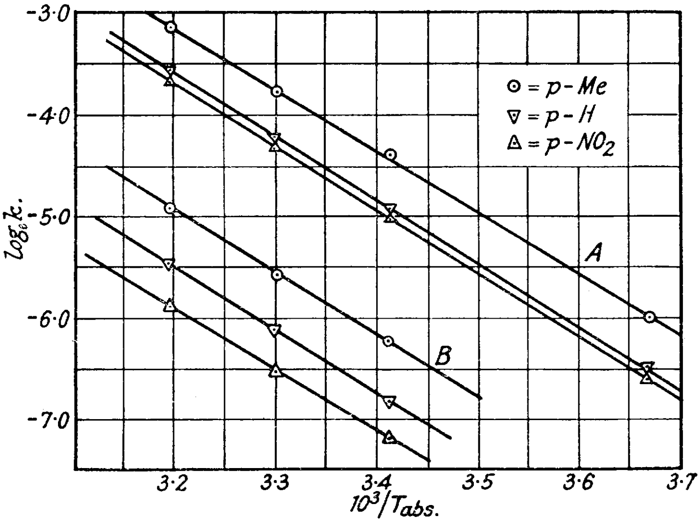
Determination of the Velocity Coefficients.—The bimolecular velocity coefficient was derived from the value of $x/(a - x)t$, obtained from the slope of the best straight line of the $x/(a - x)$–t graph. In all cases, deviation of individual values from the line was very slight (see Figs. 1 and 2) but it may be noted that at $t = 0$ the curve sometimes indicated a value of $x/(a - x)$ corresponding to about 0·2—0·4% of bromide ion. This slight deviation from the origin is almost within the range of experimental error, but the possibility of the presence of a very small initial concentration of bromide ion arising from an equilibrium $\mathrm{ArBr} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \overset{\oplus}{\mathrm{Ar}} + \overset{\ominus}{\mathrm{Br}}$, in which k_2 (and, also, k_p) is very much greater than k_1, must not be overlooked. The degree of accuracy claimed for the results is substantiated by the reproduction of one typical set of curves in each series of velocity measurements, in Figs. 1 and 2. The plot of $\log_e k_p$ against

FIG. 2.



Full curves ——— = $C_6H_4R{\cdot}CH_2Br$ + *pyridine in aqueous* 90% *acetone at* 40°.
Dotted curves – – – – = $C_6H_4R{\cdot}CH_2Br$ + *pyridine in aqueous* 90% *alcohol at* 20°.

FIG. 3.



A = *Reaction with pyridine in dry acetone.*
B = *Reaction with α-picoline in dry acetone.*

$1/T_{abs.}$ for experiments Nos. 1—12 (pyridine) and 13—21 (α-picoline) is given in Fig. 3. These curves clearly indicate the various experimental results discussed in this communication, especially the increasing differentiation between the velocities of the substituted and unsubstituted derivatives under the different experimental conditions.

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