350. *Factors Affecting -onium Salt Formation.*

By W. Cule Davies and W. P. G. Lewis.

The observations described herein constitute the first comparative measurements of the speeds of interaction of tertiary nitrogen, phosphorus, and arsenic bases with organo-halides. The influence of experimental conditions and of the structure of the organo-halide on the formation of quaternary ammonium salts has already been investigated in detail, but the relative effects of change of the nitrogen base have received scant attention ; Long (J., 1911, **99**, 2164) measured the rates of interaction of several cyclic tertiary bases of nitrogen with organo-halides, and Thomas (J., 1913, **103**, 594) considered the effect of various alkyl groups and of some nuclear substituents on the reactivities of the dialkylanilines with organo-halides. In the present work a study of the effect of changes of the positive pole-producing atom, organo-groups attached, and nuclear substituents of the tertiary base on its reactivity with simple alkyl halides has been undertaken :

$$R_n'M + R''X \longrightarrow R_n'R''\overset{+}{M}\}\overset{-}{X}.$$

Experimental.

(All thermometer readings are corrected.)

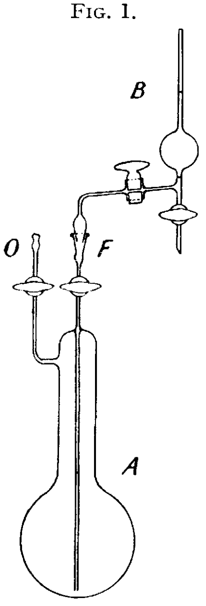
Tertiary Bases.—The amines were all carefully purified by the usual methods. The phosphines and the arsine were prepared by general methods and purified by two fractional distillations under reduced pressure in an inert atmosphere. They had the following constants : Aryldiethylphosphines : phenyl-, b. p. 120—121°/29 mm., $d_{4^\circ}^{20^\circ}$ 0·9545, $n_D^{20^\circ}$ 1·5458, $n_F^{20^\circ} - n_C^{20^\circ}$

0·0191; *p*-tolyl-, b. p. 113·5—114·5°/13 mm., $d_{4^\circ}^{20^\circ}$ 0·9373, $n_D^{20^\circ}$ 1·5428, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0176; *p*-methoxyphenyl-, b. p. 130—131°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·0015, $n_D^{20^\circ}$ 1·5498, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0196; *p*-phenoxyphenyl-, b. p. 199—200°/10 mm., $d_{4^\circ}^{20^\circ}$ 1·0743, $n_D^{20^\circ}$ 1·5968, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0233; *p*-chlorophenyl-, b. p. 129—130°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·0708, $n_D^{20^\circ}$ 1·5603, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0192; *p*-bromophenyl-, b. p. 141—143°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·2886, $n_D^{20^\circ}$ 1·5821, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0212. Phenyldiethylarsine had b. p. 104°/12 mm., $d_{4^\circ}^{20^\circ}$ 1·1960, $n_D^{20^\circ}$ 1·5630, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0197.

The alkyl halides were distilled from phosphoric oxide and then fractionally redistilled. The iodides were stored over mercury.

Solvents.—The reactions were carried out in acetone, in acetone–water (9 : 1 by vol.), and in 90% aqueous ethyl alcohol (by vol.). The acetone was purified by the method of Norris and Prentiss (*J. Amer. Chem. Soc.*, 1928, **50**, 3042); it distilled within 0·05°, and had $d_{4^\circ}^{25^\circ}$ 0·7857, $n_D^{20^\circ}$ 1·3598, $n_F^{20^\circ} - n_C^{20^\circ}$ 0·0070.

FIG. 1.



Velocity Measurements.—The reactions were all carried out at 35° ± 0·1°. Solutions of the interactants, each of concentration 0·2 g.-mol./l., were made by weighing the necessary equivalent amounts of the base and alkyl halide into flasks graduated to contain 35 c.c. at 35°, and diluting to the mark with the solvent in the thermostat. Equal volumes of the two solutions were then transferred to the reaction flask, *A* (Fig. 1), of about 80 c.c. capacity, through the ground joint *F*. The pipette, *B*, which possessed a male ground joint fitting the female joint *F* of a number of reaction flasks, enabled samples of the reaction mixtures to be withdrawn by suitable manipulation of the taps and application of slight pressure at *O*. The pipette used throughout the present measurements delivered 3·63 c.c. of liquid at 35° between the graduation marks. The measured sample was run into 20 c.c. of light petroleum, which was then repeatedly extracted with water. The aqueous extract was titrated against 0·025*N*-silver nitrate, with potassium chromate as indicator.

Results.—For a complete bimolecular reaction, $A + B \longrightarrow AB$, $k = x/at(a - x)$, where a is the initial concentration of A and B and x the concentration of AB formed after an interval t. In the present experiments, $a = 0{\cdot}1$, and the concentration of -onium salt formed after t minutes is $x = v/40 \times 3{\cdot}63$, where v is the volume (c.c.) of 0·025*N*-silver nitrate required by the 3·63 c.c. of reaction mixture delivered from the pipette.

Detailed results for one of the reactions are given in Table I; the remainder are summarised in Table II, aqueous acetone being the solvent except where otherwise denoted.

TABLE I.

Reaction between phenyldiethylphosphine and ethyl iodide.

Solvent: acetone. Temp.: 35°. Initial concentrations: 1·1630 g. phosphine, 1·0917 g. halide diluted to 70 c.c.

t, mins.	*v*, c.c.	*x*.	100*k*.	*t*, mins.	*v*, c.c.	*x*.	100*k*.
120	4·3	0·0296	3·50	465	9·0	0·0620	3·50
195	5·9	0·0406	3·51	510	9·3	0·0640	3·49
240	6·45	0·0444	3·33	555	9·6	0·0661	3·52
300	7·4	0·0510	3·46	600	9·9	0·0682	3·57
360	8·0	0·0551	3·41	10,500	14·45	0·0995	—

Mean 100*k* = 3·48.

Generally, the mean velocity coefficient for a reaction was calculated from the coefficients obtained in that part of the reaction between 20% and 80% complete, but measurements were continued until 100% formation of -onium salt was observed. This procedure was not possible where the -onium salt crystallised out during the course of the reaction, and also in some of the slowest reactions. In the latter reactions (Nos. 14, 15, 21, and 31) the bimolecular velocity coefficients showed a drift which may be due to the opposing reaction, *e.g.*, $C_6H_5NR_2 + R'I \rightleftarrows C_6H_5NR_2R'\}I$. The reactions were not, however, pursued far enough to enable the equilibrium points to be determined. The velocity coefficient of the forward reaction is sufficiently closely indicated by the bimolecular coefficients corresponding to the early stages of the reaction. Another factor which may enter into these slow reactions is that of the effect of the prolonged contact with the solvent.

TABLE II.

	Reactants. Base.	Alkyl halide.	No. of dtmtns.	Mean 100*k*.	%.†
A.	*Substituted dimethylanilines.*				
1	(Unsub.)	MeI	5	2·71	
2	,,	,,	10	2·68	
3	,,	EtI	8	0·116	
4	*p*-Me	MeI	9	7·06	
5	*p*-OMe	,,	9	14·7	
6	*p*-OEt	,,	8	15·9	
7*	*p*-NO_2 ‡	,,	No reaction		
8	*m*-NO_2	,,	3	*ca.* 0·006	20
9	*p*-Cl	,,	3	0·75	
10§	,,	,,	6	0·30	80
11	*p*-Br	,,	3	0·57	40
12§	,,	,,	4	0·25	33
13	*p*-I	,,	2	*ca.* 0·55	15
B.	*Substituted diethylanilines.*			$k \times 10^5$.	
14*	(Unsub.)	EtI	6	7·3—1·8	
15	,,	,,	8	12·3—7·7	
16	*p*-OMe	,,	9	28·0	

	Reactants. Base.	Alkyl halide.	No. of dtmtns.	Mean 100*k*.	%.†
C.	*Substituted phenyldiethylphosphines.*				
17*	(Unsub.)	EtI	9	3·48	
18*	,,	,,	4	3·68	
19	,,	,,	7	6·18	
20*	,,	EtBr	3	0·23	40
21*	,,	*n*-BuBr	6	0·03—0·006	
22*	*p*-Me	EtI	6	4·94	
23*	,,	,,	13	4·91	
24	,,	,,	7	8·61	
25*	*p*-OMe	,,	7	5·53	
26	,,	,,	7	9·64	
27*	*p*-OPh	,,	5	2·56	50
28*	*p*-Cl	,,	5	1·85	
29*	*p*-Br	,,	3	1·5	60
D.					
30*	$AsPhEt_2$	MeI	7	6·65	
31*	,,	EtI	10	0·5—0·03	

* Solvent : acetone. § Solvent : alcohol–water.

† In cases where the -onium salt separated out during the course of the reaction, the approximate percentage reaction completed when crystallisation of the salt had just commenced is given in this column.

‡ The amine was not sufficiently soluble in the acetone–water mixture to make a solution of concentration 0·2 g.-mol./l.

The following salts crystallised out from the reaction mixtures when the percentage reaction completed had reached the values indicated in the last column of Table II. The crystals of the salt were collected on a filter, washed with the pure solvent from which they had crystallised, and dried in a vacuum. *m*-Nitrophenyltrimethylammonium iodide, pale yellow crystals, m. p. 187° (decomp.) (Found : I, 41·6. Calc. for $C_9H_{13}O_2N_2I$: I, 41·2%), is difficultly soluble in water and almost insoluble in acetone. p-*Chlorophenyltrimethylammonium iodide,* glistening leaflets, m. p. 200—202° (decomp.) (Found : I, 42·7. $C_9H_{13}NClI$ requires I, 42·7%). The methiodides of *p*-bromo- and *p*-iodo-dimethylaniline have m. p. 190—193° (decomp.) and 185—200° (decomp.), respectively. *Phenyltriethylphosphonium bromide,* prisms, has m. p. 187—188° (Found : Br, 29·1. $C_{12}H_{20}BrP$ requires Br, 29·1%). p-*Phenoxyphenyltriethylphosphonium iodide* forms columns, m. p. 181—182° (Found : I, 30·6. $C_{18}H_{24}OIP$ requires I, 30·6%). *p*-Bromophenyltriethylphosphonium iodide, hexagonal leaflets, has m. p. 182° (Found : I, 31·8. Calc. for $C_{12}H_{19}BrIP$: I, 31·6%).

Phenyltriethylphosphonium iodide, prisms, m. p. 139° (Michaelis, *Annalen*, 1876, **181**, 356, gave 115°) (Found : I, 39·6. Calc. for $C_{12}H_{20}IP$: I, 39·4%), crystallised during the course of the reaction between ethyl iodide and phenyldiethylphosphine in acetone solution (concentrations, 0·25 g.-mol. of each reactant per l.). *p*-Methoxyphenyltrimethylammonium iodide, needles, m. p. 257° (Found: I, 43·3. Calc. for $C_{10}H_{16}ONI$: I, 43·3%), crystallised out almost immediately after solutions of its generators in acetone were mixed (usual concentrations).

DISCUSSION.

Factors operating in the Formation of -Onium Salts.—I. *The positive pole-producing element.* Variation of the central element in the phenyldiethyl bases produces a marked

TABLE III.

Triphenyl base.	Reaction with methyl iodide.	Reference.	$\mu \times 10^{18}$, e.s.u.*
Amine	None	Haeussermann, *Ber.*, 1901, **34**, 40.	0·26
Phosphine	Violent	Michaelis and Gleichmann, *Ber.*, 1882, **15**, 803; Michaelis and von Soden, *Annalen*, 1885, **229**, 310.	1·45
Arsine	Reacts at 100°	Michaelis, *ibid.*, 1902, **321**, 166.	1·07
Stibine	None	Michaelis and Reese, *ibid.*, 1886, **233**, 53.	0·57
Bismuthine	None		0

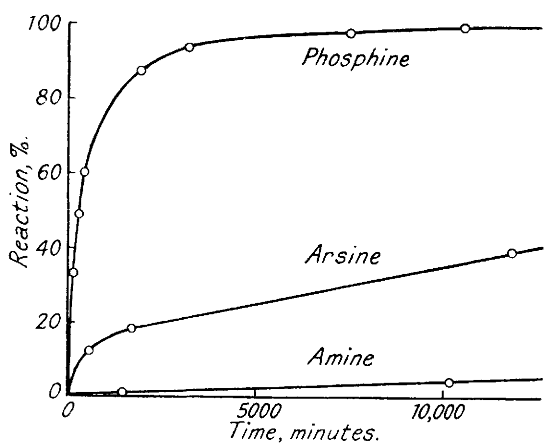
* Bergmann and Schutz, *Z. physikal. Chem.*, 1932, *B*, **19**, 401.

change in their reactivity with ethyl iodide (Fig. 2). The reactivity of the bases is in the order amine < arsine < phosphine.

Again, Table III shows, in a qualitative manner, that towards methyl iodide the phosphine has the maximum reactivity of the triphenyl bases derived from the elements of Group V*b*. Furthermore, the reactivity of the bases follows strictly the order of their dipole moments, since the lower stibines do form methiodides, whereas no bismuthine is known to combine with methyl iodide. It may be inferred, therefore, that in these cases the polarisation of the bases due to the central element determines their reactivity towards alkyl halides. The decreasing reactivity towards alkyl halides of the organic bases, phosphine to bismuthine, may be accounted for by the increasing inertness of the lone pair of electrons in passing from phosphorus to bismuth, since the formation of an alkiodide is presumably effected by the donation of the lone pair of the central atom to the alkyl radical of the organo-halide. The anomalous position of the tertiary amine, both in the velocity measurements and in the dipole moments, is striking. Moreover, examination of other chemical and physical properties of the Group V*b* elements and their compounds shows that generally nitrogen is the unique element of the family, whereas the remaining four members form a group showing a regular gradation in properties.

FIG. 2.

Reaction between phenyldiethyl bases and ethyl iodide in acetone.



II. A. *Organic radicals attached to the positive pole-producing element.* If the rate of formation of a quaternary salt depends on the ease with which the lone pair of electrons of the base is transferred to the alkyl radical of the organo-halide, then, on electronic views, diethyl- should be more reactive than dimethyl-aniline. Since the reverse order of reactivity is actually found, it seems clear that the volumes of the groups under consideration, and not their polar effects, determine the reactivities of the compounds. On the other hand, the inductive effects of the alkyl groups appear to determine the strengths of the compounds as bases, for diethyl- is a stronger base than dimethyl-aniline. The formation of a basic hydroxide and of a quaternary salt depends on the co-ordination in the former case of hydrogen, and in the latter, of an alkyl group through the lone pair of the tertiary base. Therefore, explanation of the fact that the polar effects determine the strengths of the bases and that stereochemical effects control the reactivity of the bases in the formation of quaternary salts, may lie in the difference in volume between the hydrogen atom and the alkyl group.

B. *Nuclear substituents in the phenyldialkyl bases.* Such substituents, at least in the *m*- and *p*-positions, are too far removed from the central atom to exhibit steric effects. They should, therefore, influence the reactivity of the bases according to their polar effects. The reactivity of the base is increased by electron-releasing groups (*p*-Me) and diminished by electron-attracting groups (*p*-NO_2). The order of decreasing reactivities of the aryldialkyl bases is as follows: *p*-phenetyl- > *p*-anisyl- > *p*-tolyl- > phenyl- > *p*-chlorophenyl- > *p*-bromophenyl- > *p*-iodophenyl- > *m*-nitrophenyl- > *p*-nitrophenyl-.

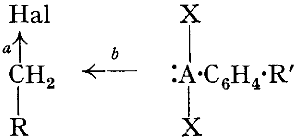
The high reactivity caused by the introduction of the *p*-alkoxyl group is undoubtedly due to the operation of its $+ T$ effect, which completely overshadows its $- I$ effect. On the other hand, the introduction of the *p*-phenoxyl group ($- I + T$) (Table II, No. 27) causes a diminished reactivity in phenyldiethylphosphine which can be explained as follows: the oxygen atom in diphenyl ether is conjugated on both sides, so that the $+ T$ effect has to be shared over two aromatic systems, and, therefore, the electronic effects observed at each *p*-position will be weakened.

The position of the *p*-halogeno-compounds as a group in the series of reactivities is such as would be expected from the observed effects of the *p*-methyl and the *p*-nitro-group, but the order of the halogens within the group, Cl > Br > I, is that of electron affinity of the substituents, and is therefore anomalous. The factor which is operating here in opposition to the inductive effect must be the electromeric effect ($+ T$).

Comparison of the velocity coefficients of the nuclear-substituted phenyldialkylamines with those of the corresponding phosphines brings out some interesting facts. The general effect of the substituents in the phosphines is in the same direction as in the amines, but is always diminished in intensity; for instance, the increase in reactivity due to the introduction of a *p*-methyl group in the amine is almost twice as much as that due to the same group introduced into the phosphine. Furthermore, the decrease in reactivity due to the substitution of a *p*-chloro-group in the amine is nearly twice that in the phosphine. The ratio of the velocity coefficients (*p*-Cl substituted compound)/(*p*-Br substituted compound) is practically a constant, 1·2—1·3, whether with amine or with phosphine in any of the solvents employed. It also appears that the damping of the effects due to the *p*-methoxyl substituent in their transmission through the heavier phosphorus atom is greater than that for the *p*-methyl group.

III. *The organo-halide.* The substitution of an alkyl radical heavier than methyl causes a diminution in the rate of addition of the alkyl halide to the base. The change from methyl to ethyl produces a much greater diminution than a change from any other radical to the next higher one. The relative effects of changing the alkyl halide from one with methyl to one with ethyl seem to be nearly the same with different bases. The conclusion of Preston and Jones (J., 1912, **101**, 1930), that the relative reactivities of organo-halides with bases (nitrogen bases, ethyl sodioacetoacetate, and sodium ethoxide) are in the main independent of the base, is thus supported. Finally, iodides are more reactive than bromides.

Mechanism of -onium Salt Formation.—With the experimental evidence now made available, Baker's mechanism (J., 1932, 1148, 2361; 1933, 1128) for the interaction between benzyl or phenacyl halides and pyridine may be extended to deal generally with -onium salt formation. The formation of an -onium salt involves two stages: (*a*) the anionisation of the halogen atom of the organo-halide, and (*b*) the co-ordination of the base by means of its lone pair to the methylene group of the organo-halide:



$$\begin{array}{ccc} \text{Hal} & & \text{X} \\ {}^{a}\uparrow & & | \\ \text{CH}_2 & \xleftarrow{b} & \colon\!\text{A}\cdot\text{C}_6\text{H}_4\cdot\text{R}' \\ | & & | \\ \text{R} & & \text{X} \end{array}$$

Considering first the base, it is clear that the most reactive will be that possessing the greatest ease of donating its lone pair of electrons. Amongst the bases of the Group V*b* elements, this will be the phosphine (cf. Table III, dipole moments). Although the effects of radicals X immediately attached to the central atom are largely steric, where the polar substituent, R′, is situated at a sufficiently large distance from the central atom, the reactivity of the base is increased by electron-releasing and decreased by electron-attracting groups. This is to be expected, since any flux of electrons from radicals attached to the central atom towards the lone pair should facilitate stage (*b*). Moreover, as has been found, the intensity of the polar effects should be lessened by an increase in the weight of the central atom.

The reactivity of the alkyl halides towards the tertiary bases is in the order $CH_3 > C_2H_5 > (CH_3)_3C$, and bromoacetic acid is more reactive towards pyridine than *n*-propyl bromide (Clark, J., 1910, **97**, 416). Therefore, in the present cases, (*b*) must be the principal rate-determining stage, since an electron-attracting group R in the alkyl halide, causing an electron deficiency around the methylene group, assists stage (*b*), even though it tends to retard stage (*a*).

The application of the mechanism to the influence of the halogen atom of the alkyl halide has been considered by Baker.

The authors thank the Chemical Society for a grant.

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF.

[*Received, August* 16*th*, 1934.]