340. *The Basic Strengths of Tertiary Amines, Phosphines, and Arsines.*

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The dissociation constants of a number of bases in solution in 30% or 50% ethyl alcohol have been computed from the results of potentiometric titrations with hydrochloric acid at 20° employing a glass electrode. The following are the principal results. (1) Phenyldimethylphosphine is a slightly stronger base than dimethylaniline, whereas phenyldimethylarsine is a very weak base. This is not the sequence expected from the results of measurements of the velocity of interaction between these bases and alkyl halides: phosphine > arsine > amine. (2) Phenyldiethylphosphine is a slightly stronger base than phenyldimethylphosphine, but diethylaniline is much stronger than dimethylaniline. These results should be compared with the feeble reactivity of diethylaniline towards alkyl halides. (3) Methyl substituents in the *o*-position of the phenyldialkyl bases increase the strength of the base. Thus dimethylmesidine was one of the strongest tertiary aromatic amines investigated. On the other hand such substituents diminish the reactivity of the base towards alkyl halides. (4) A linear relation exists between the p_K of dimethylaniline and its *p*-substituted derivatives and the logarithm of the velocity coefficient of the reaction between the amine and methyl iodide. (5) The effects of nuclear substituents are generally weaker in the phosphines than in the amines.

A noteworthy feature of the chemistry of the Group V*b* elements is the very feebly basic character of phosphine and arsine relative to ammonia. No comparisons have hitherto been made of the basic strengths of tertiary organic amines, phosphines, and arsines. In view of recent results, mentioned below, on the reactivities of such tertiary compounds, measurements have now been made of their dissociation constants. The reactivity of a tertiary phosphine towards alkyl halides is much greater than that of the corresponding arsine, which in turn is greater than that of the amine (Davies and Lewis, J., 1934, 1599; Davies, J., 1935, 462). Further, tertiary phosphines show considerable activity in combining with *p*-benzoquinone and carbon disulphide, whereas amines and arsines only possess this power to a small degree (Davies, J., 1935, 1786). The facile oxidation of tertiary phosphines compared with tertiary amines is another example of the high reactivity of tertiary phosphines. Attempts were made to connect this remarkable activity of the tertiary phosphine with its dipole moment, which is by far the largest in a series of corresponding tertiary organic compounds derived from the Group V*b* elements: the dipole moments of the hydrides are in the order $NH_3 > PH_3 > AsH_3$. A satisfactory explanation of this difference arising from the substitution of organic groups into ammonia and phosphine is still lacking.

The method adopted for the measurement of the dissociation constants was an electro-

metric titration at 20° of the base in solution in 30% or 50% alcohol with standard hydrochloric acid in the same solvent, a glass electrode being used, with a saturated potassium chloride–calomel half cell as reference electrode. The procedure was almost identical with that of Bennett, Brooks, and Glasstone (J., 1935, 1821). We have preferred, however, to give our results as $p_K = p_H + \log C_{salt}/C_{base}$, or, where $p_H < 4$, the form corrected for hydrolysis, $p_K = p_H + \log \{(C_{salt} - [H^+])/(C_{base} + [H^+])\}$, rather than make any assumptions as to the values of p_K for water in the aqueous alcohols.

Dissociation Constants of Bases at 20°.

	30% Alcohol.				50% Alcohol.			
Base.	G. base/100 c.c.	Normality of HCl.	Mean p_K.	Mean variation from mean p_K.	G. base/100 c.c.	Normality of HCl.	Mean p_K.	Mean variation from mean p_K.
Dimethylaniline	0·1211	0·02	4·71	± 0·06	0·2411	0·0501	4·21	± 0·015
	0·2422	0·04	4·81 (4·76)	0·02				
	0·2422	0·04	4·71	0·02				
	0·0605	0·005	4·79	0·02				
Dimethyl-*o*-toluidine	0·0676	0·01	5·42	0·02	0·0676	0·01	5·07	0·025
	0·0338	0·005	5·42 (5·42)	0·02				
Dimethyl-*m*-toluidine	0·0676	0·01	4·86	0·01	—	—	—	—
	0·0338	0·005	4·86 (4·86)	0·01				
Dimethyl-*p*-toluidine	0·0676	0·01	5·31	0·03	0·0676	0·005	4·77	0·02
	0·0338	0·005	5·26 (5·29)	0·03				
o-Methoxydimethylaniline	—	—	—	—	0·1511	0·02	5·49	0·01
p-Methoxydimethylaniline	0·1511	0·04	5·47	0	0·1511	0·02	5·16	0·02
	0·1511	0·02	5·56 (5·53)	0·06				
	0·3023	0·04	5·55	0·03				
p-Ethoxydimethylaniline	0·1652	0·02	5·59	0·02	—	—	—	—
	0·3303	0·04	5·59 (5·59)	0·02				
p-Nitrosodimethylaniline	—	—	—	—	0·0300	0·002	3·52	0·05
p-Fluorodimethylaniline	0·0348	0·005	4·49	0·02	0·0695	0·01	4·01	0·05
	0·0695	0·01	4·49 (4·49)	0·015				
p-Chlorodimethylaniline	0·0311	0·005	3·80	0·04	0·0778	0·01	3·45 (3·33)	0·03
					0·0389	0·005	3·21	0·02
p-Bromodimethylaniline	—	—	—	—	0·0500	0·005	2·82	0·02
p-Iododimethylaniline	—	—	—	—	0·0618	0·005	2·73	0·01
Dimethylmesidine	—	—	—	—	0·2310	0·02	5·13 (5·15)	0·01
					0·1226	0·02	5·17	0·01
Diethylaniline	—	—	—	—	0·0749	0·01	5·85	0·02
p-Nitrosodiethylaniline	—	—	—	—	0·0356	0·002	3·56	0·04
Di-*n*-butylaniline *	—	—	—	—	—	—	4·84	—
Phenyldimethylphosphine	—	—	—	—	0·0472	0·01	4·33 (4·32)	0·08
					0·0449	0·01	4·31	0·10
p-Tolyldimethylphosphine	—	—	—	—	0·1360	0·02	4·66	0·15
p-Xylyldimethylphosphine	—	—	—	—	0·1104	0·01	4·38 (4·40)	0·15
					0·1701	0·02	4·43	0·15
Mesityldimethylphosphine	—	—	—	—	0·0920	0·01	6·49 (6·51)	0·05
					0·1695	0·02	6·53	0·01
Phenyldiethylphosphine	—	—	—	—	0·0890	0·01	4·29	0·10
					0·0520	0·01	4·49 (4·37)	0·11
					0·0421	0·005	4·34	0·08
Phenyldi-*n*-butylphosphine †	—	—	—	—	—	—	3·80	—
Mesityldimethylarsine	—	—	—	—	0·1074	0·01	2·11	0·10

Phenyldimethyl-, phenyldiethyl-arsine, *p*-dimethylaminobenzaldehyde, *m*-, *p*-nitrodimethylaniline and *p*-nitrodiethylaniline were too weak to be measured accurately by the present method.

* Single determination of the p_H of 0·1049 g. of the base and 35 c.c. of 0·02*N*-hydrochloric acid diluted to 100 c.c. with solvent.

† Single determination of the p_H of 0·1538 g. of the base and 30 c.c. of 0·02*N*-hydrochloric acid diluted to 100 c.c. with solvent.

The opportunity has also been taken of measuring the dissociation constants of a number of substituted dimethylanilines, in view of the paucity of results hitherto obtained.

The table gives a full list of the results now obtained. The value of p_K given is the mean of four or five determinations with successive amounts of hydrochloric acid in a titration.

In view of the almost non-basic character of phosphine, it was remarkable to find that the basic strength of a tertiary phosphine was comparable with that of an amine. In the simplest case, phenyldimethylphosphine is actually a slightly stronger base than dimethylaniline. In other cases, the size of the central atom seems to play a part, for example, in damping the effect of a nuclear substituent, but even then the strengths of amine and phosphine are not very different. Tertiary arsines, on the other hand, are extremely weak bases. Phenyldimethyl- and phenyldiethyl-arsines were too weak to be measured by the present method. Mesityldimethylarsine, the dissociation constant of which was measured, is notably weaker than dimethylmesidine. Thus the substitution of organic groups for hydrogen in phosphine enhances the basic strength to a greater extent than it does in ammonia, for ammonia is already relatively to phosphine a strong base. Explanation is as yet obscure, since it would be expected on account of the greater size of the phosphorus atom than the nitrogen atom that the availability of the lone electron pair of the central element due to the electronic effects of the attached organic groups would be slightly smaller in the phosphine than in the amine. Our results show that increase in the size of the central atom causes a diminution of the polar effects of the attached groups at the point of reaction, but that this circumstance must be of relative unimportance compared with some other factor operating when organic groups are substituted into ammonia or phosphine.

The order of reactivity of the tertiary bases with alkyl halides, phosphine > arsine > amine, is not the order of their basic strengths, which is amine and phosphine almost equal and much stronger than the arsine. Possibly the mechanisms of formation of a basic hydroxide and of an alkylhalide are different, but also some factors may be more prominent in the one than in the other; for instance, certain steric effects may be absent in the basic hydroxide formation but present in the formation of the quaternary salt.

Organic Substituents attached to the Central Atom.—No satisfactory explanation has been given of the fact that diethylaniline is a much stronger base than dimethylaniline: on electronic grounds it should be only slightly stronger. Phenyldiethylphosphine is only slightly stronger than phenyldimethylphosphine. It might appear that the anomaly has disappeared, but it should be remembered that the electronic effects of the ethyl groups should be less in the phosphine than in the amine owing to the increased size of the central atom. Support is given to this conclusion by comparing the strengths of phenyldi-*n*-butyl-amine and -phosphine with the lower phenyldialkyl-amines and -phosphines. The reactivity of dimethylaniline towards alkyl halides is much greater than that of diethylaniline (see, for example, Davies and Lewis, *loc. cit.*), so it must be concluded that steric effects in this case are more important than polar effects.

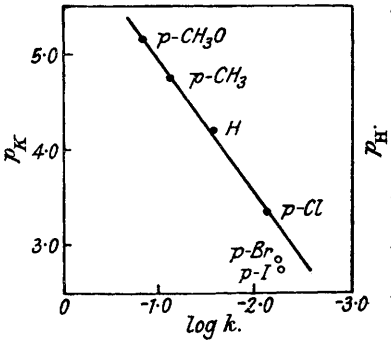
o-*Substituents in the Phenyldialkyl-bases.*—Examination of the dissociation constants of the bases with *o*-nuclear substituents shows that steric effects are probably absent. An *o*-methyl group in dimethylaniline increases the basic strength of the unsubstituted base, even more than does a *p*-methyl substituent. Only a slight increase arises from a *m*-methyl substituent. Similar effects appear to be present in the phosphines, but to a smaller extent. Thus, *p*-xylyldimethylphosphine is only a slightly stronger base than phenyldimethylphosphine, that is, the *m*-methyl group, as in the amines, has only a small effect, and also the *o*-methyl group has only a slight activating effect.

These results are sharply contrasted with the reactivities of bases towards alkyl halides (Thomas, J., 1913, **103**, 594; Davies and Lewis, *loc. cit.*). A *p*-methyl group increases the reactivity of the unsubstituted base, but an *o*-methyl group causes a notable decrease in its reactivity. Whereas polar factors decide the strength of the compound as a base, the steric factor is uppermost in determining its reactivity towards alkyl halides. Steric factors are practically absent in the *m*- and *p*-substituted compounds both in basic hydroxide and in quaternary salt formation. The difference observed between the effect of the *o*-methyl groups on the formation of the basic hydroxide and the quaternary salt is due to the difference in size of the hydrogen atom and the alkyl group which are co-ordinated by the tertiary compound.

The non-reactivity of dimethylmesidine towards methyl iodide (Hofmann, *Ber.*, 1872, **5**, 718) is a classic example of steric hindrance. Hofmann's method of attempting to obtain the salt was incorrect, *viz.*, heating the generators in a sealed tube at 150°, since such treatment would tend to decompose any salt formed, the formation of quaternary salts being in general a reversible reaction (Davies and Cox, this vol., p. 618). Nevertheless, the lenity of the formation of the methiodide is beyond question. At room temperature a mixture of the amine, excess of methyl iodide, and anhydrous ether only deposited a trace of a crystalline substance after 2 months. On the other hand we now see that dimethylmesidine is a base stronger even than dimethyl-*o*-toluidine. Only a small quantity of mesityldimethylphosphine was available and without further confirmation we do not attach any great significance to the very high result obtained. It has already been mentioned that mesityldimethylarsine is the strongest aryldialkylarsine we have investigated.

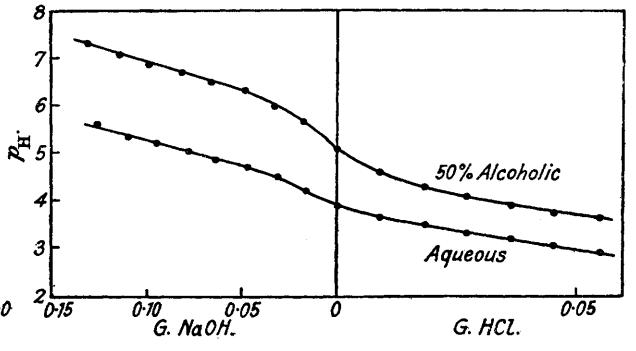
An important difference will be noted in comparing the strengths of the primary and the secondary aromatic bases with the tertiary phenyldialkyl-bases. The order of strengths of the primary bases is *o*-toluidine < aniline < *m*-toluidine < *p*-toluidine, and that of the secondary bases is similar, methyl-*o*-toluidine < methyl-*m*-toluidine < methyl-*p*-toluidine.

FIG. 1.



Dissociation constants and velocity coefficients of reaction with methyl iodide of p-*substituted dimethylanilines.*

FIG. 2.



p_H *values of aqueous and* 50 *per cent. alcoholic solutions of potassium hydrogen phthalate + hydrochloric acid or sodium hydroxide. The acid was added as a* 0·05N-*solution in each case, and the alkali as a* 0·079N-*solution in the aqueous medium and as a* 0·082N-*solution in the alcoholic medium, to* 75 *c.c. of* 0·05M-*potassium hydrogen phthalate.*

With the dimethyltoluidines, however, we have $o > p > m >$ dimethylaniline. Following Bennett and Mosses (J., 1930, 2364) the postulation of a direct effect of the *o*-methyl group of sign opposite to its usual polar effect would explain the weakness of *o*-toluidine and methyl-*o*-toluidine. However, this suggestion does not explain the great strength of dimethyl-*o*-toluidine. The results suggest that in the primary and the secondary bases the hydrogen attached to the nitrogen atom is involved in some way with the *o*-substituent, but a precise formulation is difficult. The sequences observed are not confined to a methyl substituent. For instance, Hall and Sprinkle (*J. Amer. Chem. Soc.*, 1932, **54**, 3469) gave the following order of strengths : *o*-anisidine < aniline < *p*-anisidine, and the present work gives dimethyl-*o*-anisidine > dimethyl-*p*-anisidine > dimethylaniline.

p-*Substituents in the Phenyldialkyl-bases.*—The following is the order of strengths of the *p*-substituted phenyldimethylamines : EtO>MeO>Me>H>F>NO>Cl>Br>I>NO_2. In the *p*-alkoxy-compounds it must be the electromeric effect which operates in determining the basic strength. The position of the nitroso-group indicates that it is the displacement $-N\overset{\curvearrowright}{=}O$ which operates in determining the effect of this group on the basic strength of dimethylaniline (cf. Robinson, *Chem. and Ind.*, 1925, **44**, 456). In the phosphine series the effects of *p*-substituents are in the same direction, but are generally weaker, since the electronic effect of the substituent is not transmitted so well through the heavier atom. A similar conclusion was reached by Davies and Lewis (*loc. cit.*) from a comparison of the rates of addition of alkyl halides to *p*-substituted phenyldialkyl-amines and -phosphines.

Since steric effects due to the *p*-substituent should be negligible, a simple relation between the reactivity, for instance, towards methyl iodide, of a series of *p*-substituted dimethylanilines and their dissociation constants is to be expected (see Hammett, *Chem. Reviews*, 1935, **17**, 125). A straight line (Fig. 1) is obtained when the values obtained by Davies and Lewis for log $k_{35°}$ (bimolecular velocity coefficient) for the reaction between methyl iodide and *p*-substituted dimethylanilines in 90% acetone are plotted against the p_K (50% alcohol) of the bases. The *p*-bromo- and *p*-iodo-bases show slight deviations, but in these cases the velocity coefficients are probably only approximate owing to the experimental difficulties mentioned by Davies and Lewis.

Experimental.

Materials and Procedure.—Dimethyl- and diethyl-aniline and the *N*-dimethyltoluidines were purified by treatment with acetic anhydride and fractionation. Dimethyl-*p*-anisidine and dimethyl-*p*-phenetidine were prepared by the method of Davies (*Bull. Soc. chim.*, 1935, **2**, 295), and the *p*-halogenodimethylanilines by that of Davies and Cox (*loc. cit.*). *p*-Nitroso-dimethyl- and -diethylaniline were recrystallised from acetone.

Di-*n*-butylaniline was prepared as follows: a mixture of aniline (31 g.), *n*-butyl iodide (123 g.), sodium hydroxide (27 g.), and *n*-butyl alcohol (120 g.) was heated for 12 hours at 160—180° in an autoclave. The product was steam-distilled, the oil treated with acetic anhydride, and the mixture fractionated under reduced pressure. The amine fraction was redistilled, yielding 40 g., b. p. 270° (corr.) (Reilly and Hickinbottom, J., 1917, **111**, 1016; 1918, **113**, 99, gave b. p. 260—263°).

Nitromesitylene (" Organic Syntheses," Vol. XIV) was reduced by means of tin and boiling concentrated hydrochloric acid. The product was diluted with water, made alkaline, and steam-distilled. The aminomesitylene was methylated by Sudborough and Roberts's method (J., 1904, **85**, 236), and the dimethylmesidine purified by treatment with acetic anhydride, steam-distillation, and fractionation.

Tertiary phosphines and arsines were purified by two distillations under reduced pressure, great care being taken to exclude air throughout their preparation and subsequent manipulations.

30% or 50% Alcohol was made by diluting 30 or 50 vols. of absolute ethyl alcohol to 100 vols. with water.

Solutions were made by weighing the bases into graduated flasks and diluting them with solvent, vigorous shaking and sometimes the use of slightly warmed solvent being necessary; generally solutions more concentrated than *M*/100 could not be obtained, and sometimes *M*/500 was the strongest solution obtainable. Phosphines and arsines were weighed in small capillary-necked tubes, which were filled and sealed immediately after the final distillation of the base. The tube was then broken under the solvent in a stoppered graduated flask. For the titration a known volume of the solution of the base was removed to a beaker, which was kept in an oil-bath at 20°. The glass electrode and the side-arm of the calomel half cell were supported in the beaker, which was open for the amines, but in the case of the phosphines and arsines was fitted with a stopper, and a current of nitrogen was passed over the surface of the solution. The *E.M.F.* of the cell was then determined, after the addition of each portion of standard hydrochloric acid, by means of a Cambridge Valve Potentiometer.

Standardisation of the glass electrode in 30% alcohol was carried out as suggested by Bennett, Brooks, and Glasstone (*loc. cit.*) with a series of buffer solutions (Britton and Robinson's mixture; J., 1931, 1456) whose p_H's had been determined by means of a hydrogen electrode. The latter was a wire form described by Lockwood (*J. Soc. Chem. Ind.*, 1935, **54**, 295T). For the standardisation of the glass electrode in 50% alcohol, a number of solutions were made by adding 0·0822*N*-sodium hydroxide or 0·05*N*-hydrochloric acid to 0·05*M*-potassium hydrogen phthalate (each in 50% alcohol). Fig. 2 gives the p_H values of the solutions, obtained with a hydrogen electrode, compared with the results for similar aqueous solutions. It will be seen that the behaviour of the salt on treatment with acid or alkali is similar with either water or 50% alcohol as medium.

The calibration of the glass electrode was checked frequently, but a good electrode remained constant for considerable periods. It was observed from many series of calibrations that the straight line obtained by plotting the p_H's (obtained with a hydrogen electrode) of a series of buffer solutions against the *E.M.F.*'s of cells containing a given glass electrode and these solutions was hardly affected by change of medium from water to 50% alcohol. The following figures can be used for an example:

Buffer solutions: 0·05*M*-potassium hydrogen phthalate + sodium hydroxide or hydrochloric acid.

Aqueous medium.

p_H of solution (hydrogen electrode)	5·58	5·19	4·86	4·48	3·86	3·65	3·34	3·05	2·91
E.M.F. of cell containing glass electrode	0·099	0·126	0·146	0·169	0·203	0·211	0·234	0·248	0·255

50% *Alcoholic medium.*

p_H of solution (hydrogen electrode)	7·30	6·85	6·46	5·99	5·04	4·58	4·08	3·77	3·65
E.M.F. of cell containing glass electrode	−0·002	0·028	0·051	0·075	0·131	0·157	0·186	0·204	0·211

The linear calibration holds fairly exactly with the present glass electrodes up to $p_H = 11$, both in aqueous solution and in 30% alcohol.

The following tables give some complete examples.

p-*Fluorodimethylaniline.*

0·0695 G. of base diluted to 100 c.c. 0·01*N*-Hydrochloric acid.

Solvent:	30% Alcohol.					50% Alcohol.				
Acid, c.c. ..	10	20	30	40		10	20	30	40	
p_H	5·08	4·69	4·325	3·865		4·65	4·24	3·89	3·51	
p_K	4·48	4·51	4·50	4·45	Mean 4·49	4·05	4·06	4·01	3·93	Mean 4·01

p-*Xylyldimethylphosphine.* 0·1104 G. of base diluted to 100 c.c. with 50% alcohol.

Mesityldimethylarsine. 0·1075 G. of base diluted to 100 c.c. with 50% alcohol.

0·01*N*-HCl, c.c.	10	20	30		10	20	30	
p_H	5·28	4·80	4·275		3·26	2·93	2·765	
p_K	4·53	4·43	4·19	Mean 4·38	2·21	2·08	2·05	Mean 2·11

It will be observed that in a titration of phosphine or arsine with acid the values of p_K are not quite as constant as in that of an amine. This is probably due to the difficulty in handling these bases. Furthermore, the glass electrode does not attain equilibrium as quickly in mixtures of phosphines or arsines and mineral acid as it does in the amine solutions.

Titration of Very Weak Bases.—The p_H's of mixtures of solutions of very weak bases and hydrochloric acid are hardly distinguishable from those of plain hydrochloric acid solutions of the same concentrations. If moderately concentrated solutions can be made, fairly accurate results may be obtained in some cases. The following table shows that the basic constant of *o*-aminobenzoic acid can be measured, but it should be pointed out that in experiment 3 the difference between the *E.M.F.*'s of a cell containing the weak base–acid mixture and one containing the acid alone is only 5 mv. No determination of the basic constant of *p*-dimethylaminobenzaldehyde was possible by the present method. Some very low values of p_K appearing in the literature and obtained by the electrometric titration method must on this account be accepted with reserve, especially where the concentrations employed have not been specifically stated.

Basic Constant of o-*Aminobenzoic Acid in* 50% *Alcohol.*

	p_H.	p_K.
(1) Equal vols. of 0·08*N*-*o*-aminobenzoic acid and 0·04*N*-HCl	2·00	1·62
0·02*N*-HCl	1·73	—
(2) Equal vols. of 0·04*N*-*o*-aminobenzoic acid and 0·02*N*-HCl	2·21	1·58
0·01*N*-HCl	2·08	—
(3) Equal vols. of 0·02*N*-*o*-aminobenzoic acid and 0·01*N*-HCl	2·40	1·55
0·005*N*-HCl	2·32	—

p-*Dimethylaminobenzaldehyde.*

Addition of 0·04*N*-hydrochloric acid to 50 c.c. of 0·02*N*-*p*-dimethylaminobenzaldehyde. Solvent, 50% alcohol.

Acid, c.c.	5	10	15	20
p_H	2·45	2·20	2·06	1·99

Addition of 0·04*N*-hydrochloric acid to 50 c.c. of 50% alcohol.

Acid, c.c.	5	10	15	20
p_H	2·45	2·18	2·04	1·99

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