

CCCXXIV.—*The Ionisation Constants of Some Chloro- and Nitro-anilines by the Partition Method.*

By GWYN WILLIAMS and FREDERICK GEORGE SOPER.

EXAMINATION of the published values for the ionisation constants of the chloro- and nitro-anilines revealed a number of discordancies. Being in need of these data for comparison with the results of equilibrium and kinetic measurements with anilides and chloroamines (Soper and Smith, J., 1928, 138; Williams, this vol., p. 37), we have determined the ionisation constants for *o*-,* *m*-, and *p*-chloro- and *o*-nitro-anilines, using a partition method (Farmer, J., 1901, **79**, 963; Farmer and Warth, J., 1904, **85**, 1713; Flürscheim, J., 1909, **95**, 718; 1910, **97**, 84) in which attention was directed to the effect of unhydrolysed salt on the distribution equilibrium and to the choice of extracting solvent when dealing with certain very weak bases. The results are shown in Table I, *v* denoting the range of dilutions (in litres) examined. The value of K_w employed in calculating K_b is that recommended by Harned (*J. Amer. Chem. Soc.*, 1925, **47**, 930), *i.e.*, $K_w = 1.005 \times 10^{-14}$ at 25°. The figures in brackets refer to $K_w = 1.18 \times 10^{-14}$ and are added for comparison with previous values, $K_b \times 10^{11}$, which are as follows: For *m*-chloroaniline 3.45 (Flürscheim, *loc. cit.*, by partition method), 4.8 (Goldschmidt and Keller, by catalytic saponification, *Ber.*, 1902, **35**, 3534); for *p*-chloroaniline 14.9 (Farmer and Warth, *loc. cit.*, by partition method), 9.9 (Flürscheim); for *o*-nitroaniline 0.00056 (Farmer and Warth), 0.0015 (Löwenherz, by a colorimetric solubility method, *Z. physikal. Chem.*, 1898, **25**, 385). Velej (J., 1908, **93**, 2122) has obtained values by an indicator method at 10–19° which are not in accord with the above, and Brönsted and Duus (*Z. physikal. Chem.*, 1925, **117**, 299) give the following values for the basic association constant (which may be identified with K_h ; compare Brönsted, *Rec. trav. chim.*, 1923, **43**, 718; *J. Physical Chem.*, 1926, **30**, 777; *Ber.*, 1928, **61**, 2049): at 18–20°, by an electrometric method, $K_h \times 10^4 = 25, 3.0, 0.98$; and at 15°, by catalysis of diazoacetic ester decomposition, $K_h \times 10^4 = 16.8, 2.9, 0.84$ for *o*-, *m*-, and *p*-chloroanilines respectively.

In Table I, K_b is the "concentration" basic dissociation constant, referring to infinite dilution, *i.e.*, $C_{\text{RNH}_2} \cdot C_{\text{OH}^-} / C_{\text{RNH}_2}$, whilst K_h is the "concentration" hydrolysis constant $C_{\text{RNH}_2} \cdot C_{\text{OH}_3} / C_{\text{RNH}_2}$. The latter is related to the thermodynamic equilibrium constant for

* When our experiments were started, no value was available for *o*-chloroaniline.

TABLE I.

Temp. $25^{\circ} \pm 0.01^{\circ}$. $K_w = 1.005 \times 10^{-14}$.

	No. of expts.	v.	Mean devn.		
			from mean.	$K_h \cdot 10^4$.	$K_b \cdot 10^{11}$.
<i>o</i> -Chloroaniline ...	4	39—89	3.3%	27.1	0.371 (0.435)
<i>m</i> -Chloroaniline ...	4	40—276	1.7	3.49	2.88 (3.38)
<i>p</i> -Chloroaniline ...	4	43—170	2.9	1.19	8.45 (9.92)
<i>o</i> -Nitroaniline.....	2	32—33	0.6	2850	0.00353 (0.00414)

the system $\text{RNH}_3^+ + \text{H}_2\text{O} + \text{Cl}' \rightleftharpoons \text{RNH}_2 + \text{OH}_3^+ + \text{Cl}'$ by equation (1),

$$K_h = K_1 \cdot f_{\text{RNH}_3^+} \cdot a_{\text{H}_2\text{O}} / f_{\text{RNH}_2} \cdot f_{\text{OH}_3^+} \cdot \dots \quad (1)$$

where the a 's denote activities, the f 's activity coefficients, and the C 's concentrations. At zero ionic strength, K_h becomes equal to K_1 . In the present experiments, unhydrolysed salt is always present (up to a maximum of 0.021*M*), but although the presence of moderate salt concentrations will cause an increase in K_b (Brönsted, *Trans. Faraday Soc.*, 1927, **23**, 416; 1928, **24**, 630; Dawson, *ibid.*, p. 640; Harned and Åkerlöf, *ibid.*, p. 666; Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 197), which may amount to as much as 40% in the presence of 0.02*M* salt (Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 930; Harned and Swindells, *ibid.*, 1926, **48**, 126; Dawson and Lowson, *J.*, 1929, 1217), the value of K_h is seen from equation (1) to be approximately independent of salt concentration, and therefore the values of K_b calculated from K_h by the relation $K_b = K_w/K_h$ will vary with salt concentration only in so far as K_w , the "concentration" ionic product for water, is affected. Thus, by assigning to K_w a value referring to pure water, we obtain values of K_b which refer also to pure water as medium.

The influence of salt concentration upon the activity coefficient of the amine RNH_2 must also be taken into account in the partition method, which estimates primarily the activity of the amine in the aqueous phase. If the distribution of the amine between aqueous solution and the extracting solvent is appreciably affected by the presence of the unhydrolysed salt, errors may appear, not only in the value assigned to the concentration of the amine, but also in that of the unhydrolysed salt, which is found by difference. This effect has been examined, and we have shown that for *p*-chloroaniline, where the unhydrolysed salt concentration is greatest, the partition coefficient between heptane and water is unchanged by salt concentrations up to and including $N/10$. The results are shown in Table II, and prove that molar concentrations of salts have a marked effect upon the partition coefficient.

TABLE II.

Partition coefficient of p-chloroaniline between heptane and aqueous salt solutions at 25°.

Aqueous phase.	Individual results.	Mean partition coeff.
Pure water	4.32, 4.30, 4.30	4.31
0.01M-KCl	4.27	4.27
0.01M-KBr	4.33	4.33
0.10M-KCl	4.29, 4.31	4.30
0.10M-KBr	4.36	4.36
1.00M-KCl	5.80, 5.84	5.82
1.00M-KBr	5.18, 5.21	5.20

EXPERIMENTAL.

Materials.—*o*- and *p*-Chloroanilines were prepared by the reduction of the corresponding chloronitrobenzenes. The ortho-derivative was purified by distillation under reduced pressure, and the para-derivative by recrystallisation from aqueous alcohol. *m*-Chloroaniline and *o*-nitroaniline were pure specimens from Kahlbaum and B.D.H. respectively. Phenanthrene, used for the usual "solubility correction," was obtained from a somewhat impure commercial specimen, whose purification presented some difficulty (compare Capper and Marsh, J., 1926, 724): it was finally achieved by sublimation (m. p. of product 98—99°). The solvents employed as extractors were redistilled Kahlbaum heptane and "Pure Cryst." benzene, shown to leave a negligible residue on evaporation.

Measurements.—The method consists (a) in determining the partition coefficient of the amine between water and a second solvent, and (b) in using this result to find the amount of free amine existing in an aqueous solution of the amine hydrochloride.

The three chloroanilines were investigated by partition between 60 c.c. of benzene and 1000 c.c. of water in separating funnels of 1.5 l. capacity, placed in a thermostat at 25°. The anilines and standard hydrochloric acid solution were both weighed into the funnels, the acid being always present in excess in the hydrolysis measurements. The correction for loss of benzene due to solubility in water and evaporation was determined in the usual way by a blank partition measurement with phenanthrene, which was shown to be practically insoluble in water. The mean of four experiments gave the corrected volume of the benzene layer as 59.0 ± 0.3 c.c.

The equilibrium amount of amine in the benzene layer was estimated by transferring 50 c.c. of the benzene solution by means of a pipette into a light, weighed, 100-c.c. Duroglass beaker, which was then fitted with a cork carrying an easily detachable inlet tube (always weighed with the beaker) and an outlet tube which ended flush with the lower edge of the cork. A current of air at room

temperature was drawn through (a) concentrated hydrochloric acid, (b) a calcium chloride tube, and (c) the benzene solution of the amine in the beaker. Amine hydrochloride was precipitated from the benzene solution, and the air stream was continued until the solvent had evaporated, the time required being 8 hours for 50 c.c. of solution. Air alone was then led through for 10 minutes, and the beaker and inlet tube were dried to constant weight in a vacuum desiccator containing potassium hydroxide, concentrated sulphuric acid, and also (essential for quick "desiccation") a layer of previously roasted wood charcoal. The weights of beakers were reproducible to 0.0002 g., and test experiments on the accuracy of the method of estimation with known weights of *m*- and *p*-chloroaniline in benzene solution showed losses of amine of 0.49% and 0.45% respectively. Attempts to accelerate the evaporation of the benzene by surrounding the beaker with a heating bath were abandoned owing to loss of amine.

Modification of the Partition Method.—With certain amines, the partition method may with advantage be modified in two directions, viz., (a) choice of solvent, (b) analytical method.

(a) With some amines the use of benzene as extracting solvent leads to partition coefficients which are inconveniently high. For accuracy in measuring partition coefficients, the weight of amine in the aqueous phase should be at least approximately as great as the amount in the phase in which it is estimated, since the former has to be found by difference. With benzene, even the use of inconveniently large volumes of water does not always produce the required equality. For the hydrolysis measurements, of course, the partition coefficient must not be too small, but for very weak bases, the degree of hydrolysis of the salts is so great that sufficient free base can be extracted from the aqueous salt solution even when the partition coefficient is less than 2 (compare *o*-nitroaniline). Tetrachloroethane, hexane, and heptane were tested, and the last was found to be a very suitable extracting solvent: it is not too volatile, it does not react with the substances under investigation, it is less soluble in water than is benzene (in fact, the "solubility correction" vanishes), and finally, it gives partition coefficients of the right order for very weak bases. Partitions are conveniently carried out with this solvent in 100-c.c. standard flasks.

(b) The hydrochloride method of estimation described above, although accurate, is slow; but it is necessary for *o*-chloroaniline, since Flürscheim's picrate method fails with this substance. In applying the latter method to other bases with heptane as solvent, it was found necessary to adhere exactly to the following procedure in order to secure successful results. About 1 g. of picric acid was

heated to constant weight in a distilling flask of about 90 c.c. capacity in the steam-oven. To the weighed flask were added 5—10 c.c. of benzene, and the picric acid was dissolved by warming. To the cooled solution was added the solution of amine in heptane. The solvent was distilled off, and the flask and its contents were subsequently dried to constant weight in the steam-oven. In most cases, the final weight was perfectly constant over some hours. Two test experiments with heptane solutions of *p*-chloroaniline gave amine losses of nil and 0.39% respectively. The initial addition of benzene to the picric acid is essential, since this acid is not very soluble in heptane, and consequently no picrate is formed when the heptane solution of the amine is run in. Loss of amine then invariably occurs when the solvent is distilled off.

Experimental Results.—Two complete specimen results are given below, one for partition with benzene and one with heptane. The collected partition coefficients are shown in Table III, which also illustrates the increase in precision in using the heptane modification. Some partition measurements on benzylamine are included. The following symbols are used: c_1 and c_2 are the total initial molar concentrations of hydrogen chloride and aniline respectively, c is the equilibrium concentration of free base in the aqueous phase, and F is the partition coefficient.

o-Chloroaniline.—Partition coefficient for benzene–water.

Wt. of R·NH ₂ put in, g.	Wt. of RNH ₃ Cl from 25 c.c. benzene, g.	Wt. of base in 59 c.c. benzene, g.	Wt. of base in 1000 c.c. water, g.	F .
2.6128	1.2486	2.293	0.320	121
3.0647	1.4616	2.683	0.382	119
1.3380	0.6354	1.166	0.172	115
1.2000	0.5740	1.053	0.147	121
				Mean 119

Hydrolysis constant.

c_1 .	c_2 .	Wt. of RNH ₃ Cl from 50 c.c. benzene, g.	c .	$K_h \times 10^3$.
0.01206	0.01122	0.9800	0.001004	2.83
0.02671	0.02569	1.7694	0.001813	2.53
0.02896	0.02281	1.5084	0.001546	2.76
0.01853	0.01534	1.1706	0.001200	2.70
				Mean $K_h = 2.71 \times 10^{-3}$

o-Nitroaniline.—Partition coefficient for heptane–water.

Wt. of aniline put in, g.	0.1969	0.2526	0.3010
Vol. of heptane, c.c.	25	50	60
Vol. of water, c.c.	75	150	140
Vol. of heptane layer for analysis, c.c.	20	45	50
Wt. of aniline found, g.	0.0588	0.0849	0.1091
Wt. of base in whole heptane layer, g.	0.0735	0.0944	0.1309
Wt. in aqueous layer, g.	0.1234	0.1582	0.1701
Partition coefficient	1.786	1.789	1.794
			Mean 1.790

Hydrolysis constant.

c_1 .	c_2 .	Wt. of amine from 50 c.c. heptane, g.	c .	K_h .
0.05040	0.03086	0.0989	0.008005	0.2865
0.05040	0.03004	0.0962	0.007787	0.2830
				Mean 0.285

TABLE III.

Collected partition coefficients; temp. $25^\circ \pm 0.01^\circ$.

Benzene-water.	No. of expts.	Concentration range (aqueous phase).	Mean devn. from mean.	Partition coefficient.
<i>o</i> -Chloroaniline ...	4	0.00115 — 0.00300 <i>M</i>	1.7%	119
<i>m</i> -Chloroaniline ...	8	0.000832 — 0.00327	4.4	86.2
<i>p</i> -Chloroaniline ...	4	0.00143 — 0.00348	2.8	62.4
Benzylamine	2	0.0162 — 0.0168	1.0	4.03
Heptane-water.				
<i>p</i> -Chloroaniline ...	3	0.0114 — 0.0142	0.31	4.31
<i>o</i> -Nitroaniline.....	3	0.00764 — 0.0119	0.17	1.790
(Benzylamine.....)	1	0.0383	—	0.614)

An attempt was made to estimate the amines in heptane solution by precipitation by means of picrolonic acid, filtration through a Gooch crucible, and weighing, a method which has been employed for estimating alkaloids in organic solvents (Matthes and Rammsted, *Arch. Pharm.*, 1907, **245**, 112; Freundlich and Krestovnikoff, *Z. physikal. Chem.*, 1911, **76**, 79). For *p*-chloroaniline the results were uniformly 2% low, but for *o*-chloroaniline they were not even approximately quantitative. *o*-Chloroaniline picrolonate (decomp. 170°) and *p*-chloroaniline picrolonate (m. p. 220° , decomp.) are yellow substances, and the latter is almost insoluble in organic solvents.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

[Received, September 19th, 1930.]