

NOTES

The Estimation of Potassium in Presence of Iodide. By FRANK SWAIN HAWKINS and JAMES RIDDICK PARTINGTON.

THE estimation of potassium in presence of iodides is not easy. The cobaltinitrite method gives too high results. The chloroplatinate method cannot be used unless the iodide is first removed. When this is effected by cupric sulphate and sulphur dioxide, followed by precipitation of excess copper with sodium hydroxide, the results are low. Removal of iodide by silver nitrate, followed by hydrochloric acid to remove excess of silver, gives high results (102.3—105.4%). Reduction of the chloroplatinate obtained by any method to platinum by means of magnesium is unsatisfactory, since no specimen of magnesium used was completely soluble in hydrochloric acid. There is also the difficulty of the uncertain composition of the chloroplatinate precipitate (see Treadwell, "Quantitative Analyse," 1919, 39 ff.; the method given in the English translation is unsatisfactory). A modification of the perchlorate method was finally adopted. When an alkali iodide is evaporated to dryness with perchloric acid a sufficient number of times, the whole of the iodine can be expelled, but there is loss probably due to the fumes carrying over solid particles mechanically. Evaporation to the fuming point is insufficient. The following method gave good results. A saturated solution of potassium perchlorate in 96% alcohol is cooled to 0° and filtered. A saturated solution of sodium perchlorate is similarly prepared. The alkali iodides are dissolved in the alcohol saturated with potassium perchlorate, sufficient of the sodium perchlorate solution is added to precipitate all the potassium, and the solution is boiled, cooled to 0°, and filtered through a Gooch crucible. The precipitate is

washed with the alcoholic potassium perchlorate at 0°, dried at 360°, and weighed. This gave results of the order of 99.95% with pure potassium iodide, the only error being due to a tendency of the precipitate to adhere to glass. By this method the sources of error described by Smith and Ross (*J. Amer. Chem. Soc.*, 1925, **47**, 774) are avoided. The method can be used for any potassium salts soluble in 96% alcohol.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [Received, May 11th, 1927.]

o-Nitrobenzylphenyldimethylammonium Chloride. By HLA BAW. THE *m*- and *p*-nitro-isomerides of this compound have already been described (Wedekind, *Annalen*, 1899, **307**, 287; Peacock, *J. Soc. Dyers and Col.*, 1926, 53). When *o*-nitrobenzyl chloride and dimethylaniline in equivalent quantities were mixed and kept for some months, they slowly combined to form the *quaternary compound*, which separated in large, rhomboid crystals. These were washed with ether and recrystallised from alcohol-ether. The substance had a faintly yellow colour and turned green superficially on keeping; m. p. 99.5° (Found: Cl, 11.8, 11.6. C₁₅H₁₇O₂N₂Cl requires Cl, 12.1%).—UNIVERSITY COLLEGE, RANGOON, BURMA. [Received, April 25th, 1927.]

A Spectrographic Method for the Determination of Dissociation Constants. By R. A. MORTON and A. H. TIPPING.

IT has been shown that the visible colour of solutions of violuric acid is due entirely to the violurate ion (J., 1925, **127**, 2514). Control determinations of p_H values with the quinhydrone electrode have enabled us to arrive at the value $e = 60$ for the extinction coefficient of a gram-ion of the acid radical. Hence it follows that, with a known initial concentration of violuric acid, the equation $K = [H^+][Vi^-]/[HVi_{undiss.}] = [Vi^-]^2/([HVi_{total}] - [Vi^-])$. . (1) allows of the evaluation of the dissociation constant from a spectroscopic determination of the concentration of the violurate ion.

For example, a solution of 0.00306*N*-violuric acid in a 30 cm. cell has e max. 0.42 at the position of maximum absorption. From the relation $\log I_0/I = ecd$, $0.42 = 60 \times x \times 30$; i.e., x , the concentration of violurate ion, = 0.000233. Hence $K = (0.000233)^2/(0.00306 - 0.000233)$ or 1.92×10^{-5} .

A simple extension of this work enables us to determine the dissociation constants of weak acids which obey the dilution law: If for a mixture of violuric acid of concentration $[HVi]$ with another acid of concentration $[HA]$ the value of $\log I_0/I$ at the position

of maximum absorption is found, it is clear from the relation $\log I_0/I = ecd$ that the concentration of the violurate ion can be obtained. $[HVi]$ and $[Vi^-]$ are thus known, so that the concentration $[HVi_{undiss.}]$ of the undissociated acid follows. From equation (1) $[H^+]$ can be determined, since K is known. The mixture is electrically neutral, so that $[H^+] = [Vi^-] + [A^-] + [OH^-]$. In acid solutions $[OH^-]$ is negligible, so that $[H^+] = [Vi^-] + [A^-]$. In this equation $[A^-]$ is the only unknown quantity and can therefore be evaluated. The concentration $[HA]$ originally used is known, so that $[HA_{undiss.}] = [HA] - [A^-]$. Hence $K_{HA} = [H^+][A^-]/[HA_{undiss.}]$.

The following results were obtained :

Acid.	K .	Standard values.
Acetic	$1.5-1.8 \times 10^{-5}$ at 18°	1.82×10^{-5} at 18°
"	$1.5-1.9 \times 10^{-5}$ at 19°	"
"	$1.7-2.0 \times 10^{-5}$ at 20°	"
Chloroacetic	$1.4-1.7 \times 10^{-3}$ at 18.5°	1.55×10^{-3} at 25°
Glycollic	$1.3-1.6 \times 10^{-4}$ at 19°	1.5×10^{-4} at 25°
Salicylic	$1.0-1.2 \times 10^{-3}$ at 19°	1.04×10^{-3} at 20°

The method can also be extended to the determination of the distribution of a base between violuric acid and another weak acid. This has been verified for mixtures of acetic and violuric acids.—THE UNIVERSITY, LIVERPOOL. [*Received, December 1st, 1926.*]

Reduction Products of Some Nitro-di-p-tolyl Ethers. By JOSEPH REILLY and HERBERT S. BOYD BARRETT.

As an extension of previous work (this vol., p. 67) the preparation of 3-nitro-, 3- and 2-amino-di-*p*-tolyl ethers, the partial reduction of the 2 : 6-dinitro-compound, and the nitration of 2-nitro-di-*p*-tolyl ether are now described. The 2-diazonium chloride derivative, $C_6H_4Me \cdot O \cdot C_6H_3Me \cdot N_2Cl$, on decomposition gave a tar-like product from which di-*p*-tolylene ether, $Me \text{---} \langle \text{hexagon} \rangle \text{---} O \text{---} \langle \text{hexagon} \rangle \text{---} Me$, and chloro-di-*p*-tolyl ether were isolated in small amounts.

3-Nitro-di-*p*-tolyl ether was prepared by heating potassium *p*-tolyl-oxide (21 g.) and 4-bromo-2-nitrotoluene (27 g.) with *p*-cresol (40 g.) (solvent) and copper bronze (0.2 g.) at $230-240^\circ$ for 3 hours. On fractionation of the dried ethereal extract under diminished pressure, the 3-nitro-compound was obtained as a pale yellow oil, b. p. $206^\circ/11$ mm. (Found : N, 5.8. $C_{14}H_{13}O_3N$ requires N, 5.7%). It is freely soluble in benzene and ether, much less so in cold alcohol, and insoluble in water. Reduction with stannous chloride and hydrochloric acid gave the corresponding amine. The hydrochloride

of this was obtained in colourless needles, m. p. 190—195° (Found : Cl, 14.2. $C_{14}H_{15}ON, HCl$ requires Cl, 14.2%). The base prepared from the hydrochloride separated from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 76° (Found : N, 6.5. $C_{14}H_{15}ON$ requires N, 6.6%). It is readily soluble in benzene, ether, and acetone, less so in light petroleum, and insoluble in water. The benzoyl compound separated from light petroleum in clusters of stout needles, m. p. 107° (Found : N, 4.2. $C_{21}H_{19}O_2N$ requires N, 4.4%). 3-Aminodi-*p*-tolyl ether chloraurate is a bright yellow, crystalline solid (Found : Au, 35.1. $C_{14}H_{15}ON, HAuCl_4$ requires Au, 35.6%). The azo- β -naphthol compound separated from alcohol in red plates, m. p. 149° (Found : N, 7.8. $C_{24}H_{20}O_2N_2$ requires N, 7.6%).

2-Nitrodi-*p*-tolyl ether was similarly reduced. The 2-amino-derivative on fractionation distilled at 196—198°/13 mm. as a colourless oil, which did not solidify at -15° (Found : N, 6.3. $C_{14}H_{15}ON$ requires N, 6.6%). The hydrochloride, colourless blades, m. p. 180—184°, and the sulphate, m. p. 160—162°, were prepared. The addition of the 2-diazonium chloride solution to boiling sulphuric acid (50%), followed by distillation in a current of steam, gave a colourless oil which quickly solidified. This solid was separated by fractional crystallisation into two substances of m. p.'s 70° and 165°. The latter substance was identified as a di-*p*-tolylene ether by the method of mixed melting point. The compound, m. p. 70°, appeared to be 2-chlorodi-*p*-tolyl ether.

Partial reduction of 2:6-dinitrodi-*p*-tolyl ether between 50° and 60° with stannous chloride gave the 6-nitro-2-amino-derivative. The hydrochloride, m. p. 206—210°, crystallised from ether-alcohol in colourless rosettes. The pure base, m. p. 120—122°, obtained from the hydrochloride, separated from light petroleum (b. p. 80—100°) in light yellow needles. On diazotisation in hydrochloric acid it gave an unstable product. The azo- β -naphthol compound was obtained as a dark brown, crystalline solid, m. p. 190—200° (Found : N, 10.4, $C_{24}H_{19}O_4N_3$ requires N, 10.2%).

Nitration of 2-nitrodi-*p*-tolyl ether with nitric acid (*d* 1.5) gave mainly 3:5-dinitro-*p*-cresol, together with 2:2'-dinitrodi-*p*-tolyl ether, m. p. 126°.—UNIVERSITY COLLEGE, CORK. [Received, April 11th, 1927.]
