NOTES.

Additive Compounds of Pyridine. By SHIAM SUNDER JOSHI.

THE halogen atom in 2 : 4- and 2 : 6-dinitrohalogenobenzenes loses its reactivity towards pyridine when a methyl group is present in the *m*-position : 3-chloro-4 : 6-dinitro-, 3-bromo-4 : 6-dinitro-, and 3-chloro-2-bromo-4 : 6-dinitro-toluene all fail to yield additive compounds.

The first three of the following compounds were prepared in boiling EtOH, the others by mere heating of the components together.

2-*Bromo*-4 : 6-*dinitrophenylpyridinium chloride*, orange-yellow crystals, m. p. 224°, from C_7H_8 (Found : N, 11·5; Cl + Br, 32·0. $C_{11}H_7O_4N_3ClBr$ requires N, 11·65; Cl + Br, 32·0%). 2-*Iodo*-4 : 6-*dinitrophenylpyridinium chloride*, orange crystals, m. p. 219°, from dil. acetone (Found : N, 10·9; C, 32·2; H, 1·9. $C_{11}H_7O_4N_3ClI$ requires N, 10·3; C, 32·3; H, 1·7%). 4-*Iodo*-2 : 6-*dinitrophenylpyridinium chloride*, ruby-red crystals, m. p. 213° (decomp.), from C_7H_8 (Found : N, 10·6. $C_{11}H_7O_4N_3ClI$ requires N, 10·3%). 4-*Bromo*-2 : 6-*dinitrophenylpyridinium chloride*, dark red crystals, m. p. 212° (decomp.), from C_7H_8 (Found : N, 11·35. $C_{11}H_7O_4N_3ClBr$ requires N, 11·65%). 4-*Chloro*-2 : 6-*dinitrophenylpyridinium chloride*, orange-red crystals, m. p. 197°, from EtOH (Found : N, 13·6. $C_{11}H_7O_4N_3Cl_2$ requires N, 13·3%). 4-*Bromo*-2 : 6-*dinitrophenylpyridinium bromide*, red crystals, m. p. 193° (decomp.), from EtOH (Found : N, 10·85. $C_{11}H_7O_4N_3Br_2$ requires N, 10·4%).—MEERUT COLLEGE, MEERUT, INDIA.

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The Dissociation Constant of Acetic Acid. A Criticism. By D. J. G. IVES.

JEFFERY and VOGEL (J., 1932, 2829) have redetermined the dissociation const. of HOAc, and to obtain the equiv. conductivity at zero concn., they measure the conductivities of solutions of NaOAc and KOAc. From the latter values they subtract the conductivity of the H_2O used as solvent, and then apply a correction for hydrolysis, using the approx. relation $a_h = \sqrt{K_w/C \times K_a}$, where a_h is the degree of hydrolysis, K_w the ionic product for H_2O, K_a the approx. dissociation const. of the acid, and C the concn. of the salt.

In adopting this procedure, the authors have, apparently, overlooked the fact that the corrections for the solvent and for the hydrolysis must be considered together. It is not permissible to estimate the extent of hydrolysis whilst neglecting the presence of an acid impurity in the solution.

The equilibria in a solution of the Na salt of a weak acid containing H_2CO_3 as an impurity are as follows :

(1) $NaA = Na^{\bullet} + A'$.
(2) $H_2CO_3 \rightleftharpoons H^{\bullet} + HCO_3'$.
(3) $H_2O \rightleftharpoons H^{\bullet} + OH'$.
(4) $A' + H^{\bullet} \rightleftharpoons HA$.

All these equilibria are interdependent and must be considered together. The net effect of the hydrolysis (4) is not to increase the conductivity, but to *reduce* it. It must be remembered that the conductivity of the H_2O used as solvent is almost entirely due to $H^{\bullet}$ ions, on account of their great mobility, and that these are almost entirely removed, together with some acid anions, by the hydrolysis. The increase in the concn. of OH' ions necessary to maintain K_w const. is so small as to be insignificant.

This can be seen by solving the following equation :

$$\frac{K_w}{[H^{\bullet}]} + \frac{K_c m}{[H^{\bullet}] + K_c} + \frac{K_a M}{[H^{\bullet}] + K_a} = [H^{\bullet}] + M$$

where K_c and m are respectively the primary dissociation const. and the concn. of H_2CO_3, K_a is the dissociation const. of the acid HA, and M the total concn. of the Na salt. This equation, derived from the above equilibria, expresses the degree of hydrolysis and indicates the electroneutrality of the solution.

To consider the implications of this error, let κ_1 be the total obs. conductivity of a given solution, and κ_2 the corresponding value to which the normal H_2O correction has been applied. Jeffery and Vogel assume that the equiv. conductivity $\Lambda' = \kappa_2 \times 10^3/C$ is greater than the true equiv. conductivity, Λ, of the salt by an amount due to the presence of alkali hydroxide. Actually, Λ' is considerably *less* than the true Λ for the reasons above stated.

This error in Jeffery and Vogel's calculations accounts for the disagreement between their results for the equiv. conductivities of NaOAc and those of MacInnes and Shedlovsky (*J. Amer. Chem. Soc.*, **1932**, **54**, **1429**). As would be expected, the disagreement is greater the more dilute the solution.

In a series of determinations of mobility recently carried out by the author, the Onsager equation was used for the purpose of extrapolation to zero concn., and it was found in the majority of cases that the Λ_0 values obtained from the more dil. solutions tended to be low. When, however, instead of the usual " normal " water correction, a true water and hydrolysis correction was applied according to the above equation, concordant results were obtained down to the lowest concns. This is of interest in that the use of a recognised extrapolation equation has provided an indication of an error which, evidently, might otherwise have been missed.

Attention has already been drawn to this source of error in determinations of mobility by Davies (*Trans. Faraday Soc.*, **1932**, **28**, **607**).—IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, January* 12*th*, **1933**.]

The Determination of Copper by the Salicylaldoxime Method.

By S. ASTIN and H. L. RILEY.

THE cost of the reagent is a disadvantage in Ephraim's accurate and convenient method for the determination of Cu by means of salicylaldoxime (*Ber.*, **1930**, **63**, **1928**). The reagent can be prepared directly from salicylaldehyde and NH_2OH,HCl, however, at a very small cost, and the following expts. indicate that it is unnecessary to isolate the aldoxime.

Salicylaldehyde (2·22 g.), dissolved in 8 c.c. of EtOH, was added to an equiv. quantity (1·27 g.) of NH_2OH,HCl in 2 c.c. of H_2O, the solution diluted with 15 c.c. of EtOH, and the mixture stirred slowly into 225 c.c. of H_2O at 80°. This gave an approx. 1% solution of the reagent. The following table shows the results obtained when the above solution was employed to ppt. Cu from standard $CuSO_4$ aq. in presence of various amounts of $NiSO_4$ and HOAc. 1 G. of NaOAc was added in each expt. and the vol. of the solution from which the Cu was pptd. was 150—200 c.c.

$NiSO_4,7H_2O$ added, g.	HOAc added, c.c.	Ppt., g.	Cu found, g.
—	10	0·1172	0·0222
0·042	10	0·1175	0·0223
0·083	10	0·1178	0·0223
0·166	10	0·1176	0·0223
0·083	20	0·1180	0·0224
0·125	30	0·1180	0·0224
	Calc.	0·1177	0·0223

The wt. of ppt. obtained when excess of $CuSO_4$ aq. was added to a definite vol. of the reagent indicated that the formation of salicylaldoxime had occurred to an extent about 90% of the theor.

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3 : 5-*Dinitrobenzaldehyde*. By HERBERT H. HODGSON and ERNEST W. SMITH.

CUPROUS hydride, prepared from $CuSO_4,5H_2O$ (7 g.) in H_2O (30 c.c.) and sodium hypophosphite (10 g. in 26 c.c. H_2O and 4 c.c. conc. H_2SO_4) at 60°, was washed, drained, and allowed to react with 4-bromo-3 : 5-dinitrobenzaldehyde (10 g.), dissolved in C_6H_6 (100 c.c.), for 3 hr. at 65—70°; 300 c.c. H_2O were then added and the C_6H_6 was removed by steam-distillation. The residual liquor after filtration deposited, on cooling, 3 : 5-*dinitrobenzaldehyde*, which, after treatment with hot aq. HCl to remove Cu compounds, crystallised from H_2O in very pale yellow prisms (1·6 g.), m. p. 85° (Found : N, 14·4. $C_7H_4O_5N_2$ requires N, 14·3%). It forms in cold 5% NaOH aq. a red solution, from which it is recovered unchanged if pptd. immediately but in which it undergoes profound alteration when kept.

Derivatives.—*Semicarbazone*, very pale orange micro-needles from AcOH, m. p. 256° (Found : N, 27·8. $C_8H_7O_5N_5$ requires N, 27·7%); *oxime*, fine colourless needles from 50% aq. EtOH, m. p. 159° (Found : N, 20·1. $C_7H_5O_5N_3$ requires N, 19·9%); *phenylhydrazone*, orange micro-needles from AcOH, m. p. 210° (Found : N, 19·7. $C_{13}H_{10}O_4N_4$ requires N, 19·6%), which give no coloration with alc. NaOH and a yellowish-brown with conc. H_2SO_4; p-*nitrophenylhydrazone*, fine yellow needles from AcOH, m. p. 295° (decomp.) (Found : N, 21·0. $C_{13}H_9O_6N_5$ requires N, 21·1%), which give with alc. NaOH a red-violet colour by transmitted and a blue-violet by reflected light, also red-orange with conc. H_2SO_4; 2 : 4-*dinitrophenylhydrazone*, orange-yellow micro-needles from $PhNO_2$, m. p. 295° (Found : N, 22·5. $C_{13}H_8O_8N_6$ requires N, 22·3%), which give a cherry-red colour with alc. NaOH and a greenish-yellow with conc. H_2SO_4; p-*bromophenylhydrazone*, orange needles from AcOH, m. p. 250° (Found : Br, 21·7. $C_{13}H_9O_4N_4Br$ requires Br, 21·9%), which give no colour with alc. NaOH and a yellowish-green with conc. H_2SO_4; 3 : 5 : 3′ : 5′-*tetranitrobenzaldazine* (with hydrazine), buff micro-needles from $PhNO_2$, m. p. 303° (Found : N, 21·7. $C_{14}H_8O_8N_6$ requires N, 21·6%), which give no colour with either alc. NaOH or conc. H_2SO_4; 3′ : 5′-*dinitrobenzylideneaniline*, stout buff needles from 50% EtOH, m. p. 123° (Found : N, 15·7. $C_{13}H_9O_4N_3$ requires N, 15·5%); 3′ : 5′-*dinitrobenzylidene*-p-*toluidine*, buff plates from 70% EtOH, m. p. 160° (Found : N, 14·7. $C_{14}H_{11}O_4N_3$ requires N, 14·7%); 3′ : 5′-*dinitrostyrylquinoline* (with quinaldine in boiling AcOH), colourless micro-needles from AcOH, m. p. 270° (Found : N, 13·0. $C_{17}H_{11}O_4N_3$ requires N, 13·1%).

3 : 5-Dinitro-4-aminobenzaldehyde could not be diazotised by any of the numerous methods tried.

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