

NOTES.

The Formation of Dithionate by the Action of Pyrosulphate on Sulphite. A Reply to H. Bassett and A. J. Henry. By PAUL BAUMGARTEN.

BASSETT and HENRY mention (J., 1935, 915) that, contrary to my statement (*Ber.*, 1932, 65, 1645), they have not succeeded in obtaining potassium dithionate from potassium sulphite and potassium pyrosulphate according to the equation $\text{SO}_3'' + \text{S}_2\text{O}_7'' = \text{S}_2\text{O}_6'' + \text{SO}_4''$. The implication of their wording is that the substance, potassium pyrosulphite, from which I prepared potassium sulphite contained dithionate.

I have repeated the experiment, using potassium sulphite prepared from potassium hydroxide and sulphur dioxide. Sulphur dioxide (3.85 g.) was passed into a cooled solution of potassium hydroxide (6.75 g.) in air-free water (50 c.c.). This solution and also the other reagents showed no trace of dithionate. To the potassium sulphite solution, which was diluted to 75 c.c., potassium bicarbonate (13 g.) was added. (This quantity was enough to neutralise the potassium bisulphate contained in potassium pyrosulphate and the bisulphate which was formed in a secondary reaction by the hydrolysis of pyrosulphate, so that during the entire reaction the sulphite was present as such and not as bisulphite or pyrosulphite.) Then potassium pyrosulphate (17 g. containing about 60% of $\text{K}_2\text{S}_2\text{O}_7$) was added at 10° as described (*loc. cit.*). The mixture was stirred for 30 minutes at 10° and then for 3 hours for about 20°. During the stirring, in order to avoid auto-oxidation, the air above the reacting liquid was

displaced by a current of carbon dioxide. After completion of the reaction, the work was continued in the way previously described. The yield was the same as before, *ca.* 1 g. of potassium dithionate. This dithionate could have been neither introduced with the reagents used nor formed by auto-oxidation, because the air was expelled by means of carbon dioxide and the solution was bicarbonate alkaline until the end of the reaction.

The sulphonation of sulphite by means of pyrosulphate thus definitely proved seems, moreover, extremely probable, because sulphite can also be almost quantitatively sulphonated to dithionate by means of other substances, such as trisubstituted aminosulphonic acids (Baumgarten, *Ber.*, 1932, 65, 1645), which contain co-ordinately linked sulphur trioxide similar to that of pyrosulphate.

The failure of Bassett and Henry can perhaps be explained by lack of sufficient bicarbonate. A similar solution of potassium sulphite without the addition of bicarbonate gave, in fact, on sulphonation with potassium pyrosulphate in a similar manner to that described above, so small a quantity of dithionate that, after its hydrolysis, only a slight precipitate of barium sulphate was obtained. Owing to the bisulphate contained in pyrosulphate and that produced by the hydrolysis of pyrosulphate, the sulphite would mostly change into bisulphite before its sulphonation by the pyrosulphate. But bisulphite cannot be sulphonated to dithionate, as was shown in a further experiment in which potassium pyrosulphite could not be sulphonated by means of trimethylaminosulphonic acid, probably because in the bisulphite ion, HSO_3^- , and in the pyrosulphite ion, $(\text{O}_3\text{S}\cdot\text{SO}_3)^-$, formed from this, the central sulphur is co-ordinately saturated and therefore cannot join sulphur trioxide to dithionate as in the co-ordinately unsaturated sulphite ion SO_3^{2-} .—BERLIN UNIVERSITY. [Received, July 29th, 1936.]

The Electrolytic Reduction of Vasicine. By K. S. NARANG and J. N. RAY.

SINCE communicating the paper under this title (this vol., p. 686), we have prepared the compound described as (III), but it was found to be identical with (I). The mixed m. p. determination of the two compounds was done with the samples prepared by Juneja, Narang, and Ray (J., 1935, 1277) and the depression recorded was observed. We are reinvestigating the circumstances of the formation of (III).—UNIVERSITY CHEMICAL LABORATORIES, LAHORE. [Received, July 9th, 1936.]

Preparation of 2:6-Dinitro-p-phenylenediamine, 2:6-Dinitrotetramethyl-p-phenylenediamine, and 4-Chloro-2:3-dinitroanisole. By HERBERT H. HODGSON and J. HAROLD CROOK.

2:6-DINITRO-*p*-PHENYLENEDIAMINE was prepared by Verberg (*Diss.*, Leiden, 1933) from the difficultly accessible 4-bromo-3:5-dinitroacetanilide, but had already been obtained by the authors by the simpler process of heating 2:6-dinitro-*p*-anisidine (5 g.) in a sealed tube for 2 hours at 140° with alcohol (30 c.c.) saturated with ammonia at 0°. The product crystallised on cooling and separated from alcohol in elongated permanganate-coloured prisms, m. p. 225° (Found: N, 28.7. Calc.: N, 28.3%).

2:6-Dinitrotetramethyl-*p*-phenylenediamine was formed when 2:6-dinitrodimethyl-*p*-anisidine (Hodgson and Crook, J., 1933, 825) was heated in a sealed tube with excess of dimethylamine dissolved in alcohol. It crystallised from alcohol in long, slender, deep purple needles, m. p. 176° (Found: N, 22.3. $\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_4$ requires N, 22.0%).

4-Chloro-2:3-dinitroanisole.—Aceto-*p*-anisidide was nitrated by the method of Meldola and Eyre (J., 1902, 81, 990) using nitric acid (*d* 1.42) alone, and the 2:3-dinitro-product hydrolysed by boiling with 50% sulphuric acid. A solution of the resulting 2:3-dinitro-*p*-anisidine in boiling glacial acetic acid (40 c.c.) was (2 g.) chilled to 0° and poured gradually into a solution of sodium nitrite (0.8 g.) in concentrated sulphuric acid (8 c.c.) kept at 0°. 4-Chloro-2:3-dinitroanisole was precipitated when the diazo-solution was poured into cuprous chloride (1.5 g.), dissolved in concentrated hydrochloric acid (15 c.c.) initially at 15°; it crystallised from alcohol in colourless needles, m. p. 133° (Found: Cl, 15.1. $\text{C}_7\text{H}_5\text{O}_3\text{N}_2\text{Cl}$ requires Cl, 15.3%), which were very slowly volatile in steam.

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The System Nitrobenzene-Sulphuric Acid-Water. By KENNETH C. BAILEY
and JOHN HILTON.

IN the course of another investigation, one of the authors required information about the solubility relationships of nitrobenzene, sulphuric acid, and water. As a search of the literature failed to disclose what was required, a triangular diagram was constructed from data obtained at 17°.

Pure nitrobenzene was redistilled before use. The sulphuric acid was prepared by mixing 95% acid with pure fuming sulphuric acid, and recrystallising. It was checked by titration with *N*-alkali which had been standardised with constant-boiling hydrochloric acid.

The usual method of preparing a ternary solubility diagram, *i.e.*, analysing conjugate solutions and drawing tie-lines, was not followed, as solutions containing sulphuric acid are so hygroscopic that errors are likely to be introduced during the analytical process. Weighed quantities of two of the components were mixed, and the third (usually water) added until opalescence appeared. A perfectly sharp end-point was usually obtained. The following are the compositions (molar fractions) of mixtures lying on the solubility curve :

PhNO ₂ .	H ₂ O.	H ₂ SO ₄ .	PhNO ₂ .	H ₂ O.	H ₂ SO ₄ .	PhNO ₂ .	H ₂ O.	H ₂ SO ₄ .	PhNO ₂ .	H ₂ O.	H ₂ SO ₄ .
0.00054	0.849	0.150	0.0424	0.480	0.478	0.263	0.275	0.462	0.766	0.055	0.179
0.00084	0.807	0.192	0.0652	0.446	0.489	0.327	0.235	0.438	0.864	0.030	0.106
0.0032	0.662	0.335	0.089	0.421	0.490	0.463	0.171	0.366	0.976	0.0041	0.0202
0.0088	0.574	0.417	0.151	0.360	0.489	0.484	0.167	0.349	0.986	0.014*	—
0.0159	0.537	0.447	0.171	0.345	0.484	0.641	0.102	0.257	0.0003	0.9997*	—
0.0234	0.513	0.464	0.192	0.325	0.483						

The two results marked * were obtained from Davis's data (*J. Amer. Chem. Soc.*, 1916, **38**, 1170) for binary mixtures of nitrobenzene and water at various temperatures.

Nitrobenzene and sulphuric acid appear to be miscible in all proportions at 17°. It seemed at first as if mixtures containing only a minute amount of sulphuric acid were opalescent, but this was almost certainly due to the difficulty of preventing the acid from acquiring traces of water from the air.—TRINITY COLLEGE, DUBLIN. [*Received, July 30th, 1936.*]

The Interaction of Tetraphenylglycol and Pyridinium Chloride. By ALEXANDER SCHÖNBERG and ROBERT MICHAELIS.

TETRAPHENYLGlyCOL combines with pyridine and hydrogen chloride to give a crystalline substance, C₃₁H₂₈O₂NCl. This appears to contain one molecule each of tetraphenylglycol, pyridine, and hydrogen chloride, and it is decomposed into these compounds by the action of alkali.

The substance is probably analogous in constitution to the products of the reaction between pyridine hydrochloride with triphenylcarbinol, CPh₃·OH, C₅H₅N, HCl (Helferich and Sieber, *Ber.*, 1926, **59**, 600), and triphenylmethyl hydrogen peroxide, C₂₄H₂₂O₂NCl (Wieland and Maier, *Ber.*, 1931, **64**, 1205). The structure analogous to that proposed by Wieland and Maier (p. 1206) for their product is, however, regarded as improbable, owing to the low reactivity of the hydroxyl group in tetraphenylglycol. The compound from tetraphenylglycol is therefore best represented in the present state of our knowledge as a molecular complex, CPh₂(OH)·CPh₂·OH, C₅H₅N, HCl.

With racemates or *dl*-conglomerates of the types CRR'R''·OH and CRR'(OH)·CRR'·OH resolution should be possible by crystallisation of their molecular compounds with optically active pyridinium chloride derivatives, for the compound with the *d*-form must differ in solubility, etc., from that of the *l*-form.

Tetraphenylglycol was dissolved in benzene (thiophen-free), and dry pyridine added. An ethereal solution of hydrogen chloride was then added until the amount of deposit did not increase on further addition. The colourless deposit was at once filtered off, washed with absolute ether (in which it is almost insoluble), and crystallised from absolute alcohol, in which, at room temperature, pyridinium chloride is readily soluble, whereas the additive compound is not; m. p. 185—190° (decomp.) (Found: C, 77.15; H, 6.02; Cl, 7.41; N, 3.05. C₃₁H₂₈O₂NCl requires C, 77.24; H, 5.85; Cl, 7.36; N, 2.90%).

Decomposition with Alkali.—The crystals were treated for a short time with an aqueous solution of alkali on the boiling water-bath; an odour of pyridine was observed. After standing for 2 hours at room temperature, during which the colourless deposit was repeatedly disintegrated, the deposit was separated and crystallised from benzene. It proved to be tetraphenylglycol.—UNIVERSITY OF EDINBURGH (MEDICAL CHEMISTRY DEPARTMENT). [*Received, May 2nd, 1936.*]