

NOTES.

The Viscosities of Phosphoric Esters. By DAVID PHILIP EVANS and WILLIAM JACOB JONES.

TRITOLYL phosphate is extensively used as a plasticiser in commercial cellulose-ester lacquer work, and Littman (U.S.A. Pat. 1,589,608, 17/10/1925), who was the first to prepare tributyl phosphate, has introduced the latter ester for the same purpose. The present note gives the results of measurements of the viscosity of phosphoric esters.

The densities of the alkyl esters employed have already been given (J., 1930, 1311); those of the tri-*o*-tolyl phosphate were d_4^{25} 1.17176, d_4^{30} 1.16760, d_4^{40} 1.16044, weighings being corrected to vacuum. The method and precautions employed were identical with those of Applebey (J., 1910, 97, 2000), except that the radius of the capillary of the Ostwald viscometer was rather greater, *viz.*, 0.3 mm. instead of 0.2 mm. By preliminary experiment it was established that the product of the mean pressure producing flow and the time of flow was constant throughout the conditions obtaining in the measurements of viscosity. The values taken for the viscosity of water were those given by Barr ("Monograph of Viscometry," Oxford, 1931, p. 308).

Viscosity in centipoises.

Orthophosphate.	20°.	25°.	30°.	35°.	40°.
Trimethyl	2.258	2.030	1.822	1.663	1.523
Triethyl	1.676	1.548	1.415	1.304	1.213
Tri- <i>n</i> -propyl	2.833	2.511	2.246	2.030	1.836
Tri- <i>n</i> -butyl	3.885	3.422	3.021	2.695	2.437
Tri- <i>o</i> -tolyl	—	86.64	61.00	—	32.73

It might be added that the lowest members of the fatty acids show a minimum viscosity, similar to that of the phosphoric esters, propionic acid being the most fluid (Gartenmeister, *Z. physikal. Chem.*, 1890, 6, 524; Traube, *Ber.*, 1886, 19, 1673).—TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF. [Received, February 1st, 1932.]

The Baeyer-Drewsen Reaction. By LEONARD ERIC HINKEL, ERNEST EDWARD AYLING, and WILLIAM HENRY MORGAN.

THE Baeyer-Drewsen reaction for an *o*-nitrobenzaldehyde (*Ber.*, 1882, 15, 775, etc.) was utilised by Tiemann and Ludwig (*ibid.*, p. 3502) in proving the constitutions of the isomeric nitro-compounds formed by the nitration of *m*-hydroxybenzaldehyde and similarly by Pschorr and Sumuleanu (*Ber.*, 1889, 32, 3405) for the *o*-nitro-derivatives of vanillin. In both cases, however, the methyl ethers

of the compounds were employed in the actual tests. Ashley, Perkin, and Robinson (J., 1930, 395) record the ready formation of the dimethoxy-indigotin from the methyl ether of 6-nitrosalicylaldehyde, but record no test with the nitrosalicylaldehyde itself. No reason appears to have been advanced by any of these workers for using the methyl ether of the nitrohydroxyaldehyde, although according to Sachs and Kantorowicz (*Ber.*, 1906, **39**, 2742) the property of forming an indigotin is possessed neither by the azo-derivative nor by the *p*-hydroxy-derivative of *o*-nitrobenzaldehyde, although the *p*-nitro- and *p*-halogeno-derivatives give the reaction.

We have found that the presence of a *m*- or *p*-hydroxyl group in an *o*-nitrobenzaldehyde inhibits indigotin formation, since 6-nitro-3-hydroxybenzaldehyde, 2-nitro- and 6-nitro-vanillin do not give the reaction, whereas their methyl ethers do so readily.

This inhibition of the Baeyer-Drewsen reaction by a hydroxyl group can be correlated with the presence of anionoid oxygen leading to the complete internal satisfaction of the electron demands of the carbonyl group and a minimum kationoid character of the carbonyl carbon atom, as has been done by Hodgson and Rosenberg (J., 1930, 14) in the case of hydroxybenzaldehydes in the benzoin reaction. In the latter reaction alkoxybenzaldehydes give the condensation, comparing with the ready indigotin formation with the methoxy-*o*-nitrobenzaldehydes, but whereas the introduction of a second group, as in *p*-benzyloxy-*m*-methoxybenzaldehyde, inhibits benzoin formation, two methoxy-groups, as in the *o*-nitroveratraldehydes, do not inhibit indigotin formation.

Whilst Pschorr and Sumuleanu (*loc. cit.*) state that both 2- and 6-nitroveratraldehydes yield indigotins, according to Pisovschi (*Bull. Soc. chim.*, 1911, **2**, 548), only the 2-nitroveratraldehyde does so (compare de Lange, *Rec. trav. chim.*, 1926, **46**, 50). We find, however, that both aldehydes yield the indigotin in the normal manner. De Lange (*loc. cit.*) also asserts that the experiments of Oelker (*Ber.*, 1891, **24**, 2594) show an anomaly to exist in the piperonal series, but Jones and Robinson (J., 1917, **111**, 908) have shown that the compounds supposed by Oelker to be bromonitropiperonals are in reality bromonitrocatechol methylene ethers, the aldehyde group having been displaced during nitration.

The presence of two *o*-nitro-groups in a hydroxy-aldehyde appears to overcome the inhibiting power of the hydroxyl group, since 2 : 6-dinitroisovanillin yields an indigotin normally. This elimination of the effect of the hydroxyl group may be ascribed to the neutralisation of the electronic effects of the anionoid oxygen (+ *I* + *T*) by those of the two nitro-groups (− *I* − *T*) combined.

The Baeyer-Drewsen reaction was performed as follows : A solu-

tion of the aldehyde (0.1 g.) in acetone (2 c.c.) was diluted with water (1—2 c.c.) and 2 or 3 drops of 4*N*-sodium hydroxide added. The mixture was heated, diluted with water (a few c.c.), cooled, and filtered to isolate the indigotin. In this way positive results were obtained with 2-nitro-, 6-nitro-, and 2 : 6-dinitro-3-methoxybenzaldehydes, 2-nitro- and 6-nitro-veratraldehydes, and 2 : 6-dinitroisovanillin, and negative results with 6-nitro-3-hydroxybenzaldehyde, 2-nitro- and 6-nitro-vanillin.—UNIVERSITY COLLEGE OF SWANSEA, UNIVERSITY OF WALES. [Received, January 16th, 1932.]

The Chemical Behaviour of Ekatantalum. By ORVALD GRATIAS
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OF late little use has been made, in the elucidation of the chemical behaviour of radioactive substances, of the ease with which small quantities of these elements can be detected and recognised. This is undoubtedly in great part due to the fact that, in general, the behaviour of very small quantities of a substance bears little relation to the reactions of the same substance in bulk. Thus one of the first known reactions of radium-*E* is the readiness with which it volatilises in hydrogen (Russell and Chadwick, *Phil. Mag.*, 1914, **27**, 112); yet it would be untrue to say that the most characteristic reaction of bismuth was the ease with which it formed a hydride. We have found, however, that contrary to the generally accepted view, the properties of the element ekatantalum (best known as the single isotope protoactinium) can be satisfactorily studied with the relatively small quantities which can be extracted from 1 g. of pitchblende.

The method of experiment was as follows. The protoactinium from a small quantity of pitchblende was concentrated free from other radio-elements with a few mg. of tantalum oxide by the method of Hahn and Meitner (*Physikal. Z.*, 1919, **20**, 529). The amount of protoactinium so separated was then measured by evaporating the solution of the oxides to dryness in a small, specially made platinum dish which could be slipped into the ionisation chamber of a valve amplifier (Collie, *Proc. Roy. Soc.*, 1931, **131**, A, 541) by which the number of particles emitted by the protoactinium was registered on a counter. The ionisation chamber consisted of an insulated vertical brass cylinder which could be maintained at a potential of —800 volts relative to the internal electrode, which was insulated in a guard ring. The collecting electrode was connected to the grid of a resistance capacity amplifier of conventional design in which the last valve was of the mercury-vapour-filled type (B. T. H. Thyatron) and actuated a counter such as is commonly

used for registering telephone calls. The platinum dishes containing the preparations to be measured were placed on the base of the chamber through a simple rotary door.

In the particular experiments to be described, about 250 particles per minute were emitted, corresponding to about 10^{-9} g. of protoactinium. The reactions of the oxide were then investigated in a straightforward way using the counter, instead of visual and gravimetric methods, to detect the presence of the protoactinium; on the whole, the reactions were very definite, but when the reaction was a balanced one the proportion which reacted could easily be determined by direct counting.

For the reactions studied, *viz.*, fusions with potassium hydroxide and potassium hydrogen sulphate, and attack with hydrofluoric acid, the results obtained were in general the same as those recently described by Grosse (*J. Amer. Chem. Soc.*, 1930, **52**, 1742) using relatively large quantities (50 mg.) of the oxide.

It is the purpose of this note to point out that the adoption of the sensitive radioactive method would enable a preliminary investigation of the properties of ekatantalum to be made without having first to isolate a weighable quantity of material.—CLARENDON LABORATORY, OXFORD. [*Received, November 23rd, 1931.*]
