Reaction of Potassium Chromate with an Indium Salt

By M. F. Stubbs[1]

The yellow precipitate formed by adding a chromate to a solution of an indium salt first described by Winkler[2] has been assumed to be indium chromate,[3] although Friend[4] points out that indium chromate does not appear to have been analyzed. In view of the present availability of indium, we have now carried out this precipitation and have made observations on the resulting changes in the *p*H of the solution.

Pure indium sulfate was prepared by the method of Seward[5] using 99.98% pure indium[6] and other reagents of analytical reagent quality. To the indium sulfate at 0.02 *M* concentration having an initial *p*H of approximately 2.5 as measured with a Model No. 3 *p*H Electrometer (Coleman), calibrated against the buffer solution furnished by the manufacturer, standard 0.2222 *M* potassium chromate solution was added at room temperature in small amounts from a buret with stirring.

A definite yellow turbidity appeared at *p*H 3.30, complete flocculation of the yellow precipitate taking place at 3.36–3.42, further additions of the chromate resulting in a steady rise in the *p*H. A typical titration curve is shown in Fig. 1. The results are in agreement with the observation of Moeller[7] that attempts to bring a simple indium salt to the neutral point result in the precipitation of hydrous indium hydroxide at *p*H 3.41–3.43.

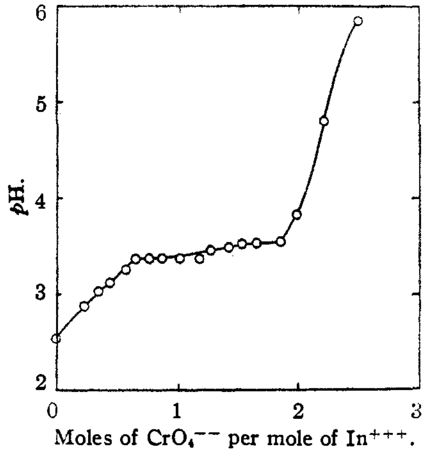

Fig. 1.

The yellow precipitate was then filtered and washed repeatedly until free of chromate. Prolonged washing, however, failed to remove the yellow color. After drying overnight at 110° to convert any hydrous indium hydroxide to indium hydroxide,[8] the precipitate was analyzed for indium by dissolving in dilute sulfuric acid and precipitating with ammonium hydroxide. This process was repeated and the indium hydroxide ignited to oxide. The combined filtrate was analyzed for chromium by acidifying with sulfuric acid, adding excess ferrous ammonium sulfate and back-titrating with standard potassium dichromate in the presence of phosphate ion with diphenylamine sodium sulfonate as indicator.

Anal. Calcd. for $In_2(CrO_4)_3$: In, 39.74; Cr, 27 02. Calcd. for $In(OH)_3$: In, 69.23. Found: In, 63.74, 63.55, 63.48; Cr, 2.16, 2.87, 2.94.

These observations indicate either that the precipitate originally formed is a mixture of indium hydroxide with indium chromate (or a basic indium chromate), or that the indium chromate as precipitated is very largely hydrolyzed during the washing process.

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[2] Winkler, *J. prakt. Chem.*, **102**, 289 (1867).

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 5, Longmans, Green and Co., 1924, p. 395.

[4] Friend, "Textbook of Inorganic Chemistry," Vol. 4, Chas. Griffin and Co., Ltd., 1917, p. 162.

[5] Seward, This Journal, **55**, 2740 (1933).

[6] From the Indium Corporation of America, Utica, New York.

[7] Moeller, This Journal, **63**, 2626 (1941).

[8] Carnelley and Walker, *Trans. Chem. Soc.*, **53**, 74 (1888).

The Viscosities of Dimethyl and Trimethylamine at 15, 25 and 35°

By Elijah Swift, Jr., and Dexter Leigh Wolfe[1]

The viscosities of dimethyl- and trimethylamine have been measured at three different temperatures using benzene as a standard.

Procedure.—A sample of the amine purified as previously described[2] was distilled into a viscometer under reduced pressure and measured under the pressure of its vapor. Benzene dried over sodium was distilled directly from the sodium into the apparatus. The values for its density and viscosity were taken from the "International Critical Tables."

An all-glass viscometer of the Ostwald type was used, its design being such that the Reynolds number was well below the critical value, and the surface tension correction[3] was minimized. The viscometer was sealed during measurements, so the upper bulb was filled by inverting the instrument beneath the surface of the water in the thermostat. It was not possible to get the same volume each time, so a correction was made for the working volume,[2] as calculated from the weight of material in the instrument and its density[1] at each temperature. At least three measurements of the time of efflux were made at each temperature, using a stop watch calibrated against a standard clock. The temperature was controlled[1] to ±0.02°. Two fillings with different material were made with each compound and with benzene.

The average difference in time between the two runs made on a liquid at the same temperature was 0.2% and the greatest difference 0.5%. The equation used to calculate the viscosities was

$$\eta = \eta_0 \frac{\mathrm{d}t}{\mathrm{d}_0 t_0} + \frac{mV}{8\pi l}\frac{\mathrm{d}}{t}\left(\frac{t^2}{t_0^2} - 1\right)$$

where the symbols have the usual meanings. The value of *m* was taken as 1.12,[4] the correction

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[1] At present with the Armed Forces.

[2] E. Swift, Jr., This Journal, **64**, 115 (1942).

[3] G. Jones and J. H. Fornwalt, *ibid.*, **60**, 1683 (1938).

[4] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922. E. Hatschek, "Viscosity of Liquids," D. Van Nostrand, Co., New York, N. Y., 1928.

amounting to about 4% at the greatest. Because of uncertainty in the value of *m* for this particular instrument, the calculated viscosities are probably reliable to only 1%.

The results obtained are given in Table I.

TABLE I

VISCOSITIES OF COMPOUNDS IN MILLIPOISES

	15°	25°	35°
Dimethylamine			
Viscosity	2.07	1.86	1.67
KE Corr.	− .06	− .06	− .07
Trimethylamine			
Viscosity	1.94	1.77	1.61
KE Corr.	− .06	− .06	− .07

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The Use of Trimethyl Phosphate as a Methylating Agent

BY A. D. F. TOY

The commercial availability of trialkyl phosphates has created considerable interest regarding their use as alkylating agents. Noller and Dutton[1] have shown that they may be used to alkylate phenols, and more recently Billman, Radike and Mundy[2] have applied them successfully to the alkylation of amines.

The present paper reports the methylation of aliphatic alcohols with trimethyl phosphate.

The reaction proceeds readily on heating, but the yield of methyl ether is only 50–60% based on the alcohol used, and not all of the available methyl groups of the phosphate ester are utilized. A fraction of the alcohol is converted into olefins and another part appears in the form of mixed alkyl acid phosphates. By employing an excess of the alkylating agent the yield of methyl ether may be increased.

With the procedures used the method is limited to alcohols boiling above 160°, because with lower boiling compounds the reaction proceeds too slowly.

TABLE I

ALKYL METHYL ETHERS

Alcohol used	Moles phosphate per mole alc.[a]	Method	Time, hr.	Yield, %	B. p., °C. (uncor.)	Ref.
2-Ethyl-hexanol-1	0.350	I	23	56.6	159–160	*b*
	.350	II	5	57.8	159–160	
	.500	II	4.5	62.0	159–160	
	.667	II	6.0	68.0	159–160	
Octanol-1	.667	II	2.0	69.5	173–174	*c*
Octanol-2	.350	I	27	56.7	159–160	*d*
Heptanol-2	.600	I	20	54.3	139–140	*e*
Hexanol-1	.350	II	9	52.7	124–125	*f*
Ethylene glycol	.333	I	5.3	37.2	122–123	*g*

[a] One and one-half moles of alcohol used in all cases. [b] Calcd. for $C_9H_{20}O$: C, 75.0; H, 13.9. Found: C, 74.4; H, 13.6. [c] Dobriner, *Ann.*, 243, 3 (1888). [d] Cerchez, *Bull. soc. chim.*, [4] **43**, 767 (1928). [e] Calcd. for $C_8H_{18}O$: C, 73.8; H, 13.85. Found: C, 73.6; H, 14.0. [f] Lespieau, *Bull. soc. chim.*, [4] **43**, 1190 (1928). [g] The compound obtained is ethylene glycol monomethyl ether: Palomaa, *Ber.*, **35**, 3300 (1902).

Experimental Part

Two general procedures were followed, both employing commercial grade trimethyl phosphate.

Method I.—The alcohol and the trimethyl phosphate were boiled under reflux until the temperature of the liquid phase reached a constant minimum. The volatile components were distilled, the last portions being removed under reduced pressure, and the desired methyl ether was isolated by careful fractionation of the distillate. The time required for the reaction was twenty to thirty hours.

Method II.—The reactants were boiled in a Claisen flask connected to a water-cooled receiver, and the temperature of both the liquid and the vapor phase was measured. After one hour the temperature of the liquid was 15–20° below the initial temperature. More heat was applied, so that the ether distilled as it was formed, and the temperature of the liquid phase was maintained 3–10° below the initial temperature. The reaction was complete when distillation ceased or when the residue began to decompose. The last traces of volatile material were removed by distillation under reduced pressure and the product was isolated as above.

The results of runs with various alcohols are listed in the table. Analyses were by Mr. Russell Bell of this Laboratory.

Among the volatile by-products, small amounts of olefins, methyl alcohol and unchanged starting material were found. The non-volatile residue was an alkali-soluble mixture of alkyl acid phosphates resembling those obtained by the action of phosphorus pentoxide on alcohols.[3]

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[1] Noller and Dutton, THIS JOURNAL, **55**, 424 (1933).

[2] Billman, Radike and Mundy, *ibid.*, **64**, 2977 (1942).

[3] Adler and Woodstock, *Chem. Industries*, **51**, 516 (1942).