[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A Convenient Procedure for the Preparation of Deuterium Chloride

BY HERBERT C. BROWN AND CORNELIUS GROOT[1]

In the course of an investigation upon which we have been engaged, the need arose for considerable quantities of deuterium chloride of high purity. Examination of the literature reveals that many methods for the preparation of the substance have been reported. In the main, however, these methods, such as the action of deuterium oxide on anhydrous magnesium chloride at 600°,[2] the reduction of silver chloride with deuterium at 700°,[3] the combination of chlorine with deuterium,[4] or the treatment of sodium chloride with deutero sulfuric acid,[5] either require the prior preparation of intermediates or involve such difficult techniques as to be unsuitable for the preparation of more than small quantities of deuterium chloride.

The procedure based on the reaction of deuterium oxide with thionyl chloride ($SOCl_2 + D_2O \rightarrow SO_2 + 2\ DCl$) has received careful attention as a means of preparing deuterium chloride in appreciable quantities,[6] and the process would be entirely satisfactory but for the difficulty involved in the separation of the product from the accompanying sulfur dioxide. In the recommended procedure, two traps cooled by dry-ice–acetone mixtures are used to remove the greater portion of the sulfur dioxide. However, since this gas possesses an appreciable vapor pressure at $-80°$ (10 mm.), it is evident that the deuterium chloride thus obtained must be contaminated with not inconsiderable quantities of sulfur dioxide. Moreover, the solubility of deuterium chloride in liquid sulfur dioxide at $-80°$ causes losses as high as 15% of the product.

In casting about for a more satisfactory procedure, we examined the possibility of utilizing benzoyl chloride for transforming deuterium oxide into the desired product. Study revealed that at somewhat elevated temperatures deuterium oxide reacts smoothly with the reagent to liberate *two* equivalents of deuterium chloride. The reaction occurs in accordance with the equations

$$C_6H_5COCl + D_2O \longrightarrow C_6H_5COOD + DCl$$

$$C_6H_5COCl + C_6H_5COOD \longrightarrow (C_6H_5CO)_2O + DCl$$

The yield of the gaseous chloride is practically quantitative, the product is analytically pure deuterium chloride, and, finally, the rate at which the gas is generated is readily controlled throughout the preparation.

The apparatus used in the preparation is shown in Fig. 1. The deuterium oxide is contained in the dropping funnel where the long length of capillary tubing serves to maintain the rate of addition of the deuterium oxide constant despite small fluctuations in pressure within the flask.

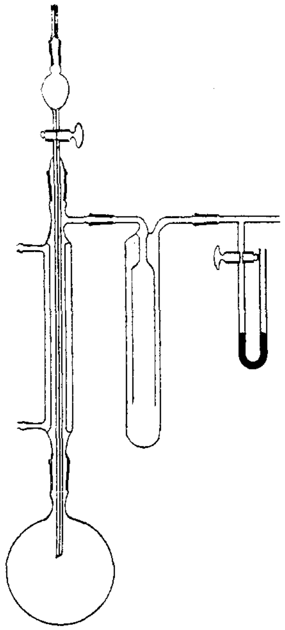

Fig. 1.—Apparatus.

The trap is immersed in an ice-bath to remove traces of benzoyl chloride which are carried past the condenser by the stream of gas. The open manometer is used to indicate the pressure at which the system is operating and to act as a safety valve should the delivery tube become blocked. It also aids in following the course of the reaction. If the delivery tube is closed momentarily (by means of a pinch clamp on a rubber connection), the action of the manometer reveals whether gas is being evolved.

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[1] This paper is taken from a dissertation submitted by Cornelius Groot to the Faculty of the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Master of Science.

[2] Lewis, MacDonald and Schutz, THIS JOURNAL, **56**, 494 (1934).

[3] Steiner and Rideal, *Proc. Roy. Soc.* (London), **A173**, 504 (1939).

[4] Bawn and Evans, *Trans. Faraday Soc.*, **31**, 1394 (1935).

[5] Frivold, Hassel and Rustad, *Physik. Z.*, **38**, 193 (1937).

[6] Langseth and Klit, *Kgl. Danske Videnskab. Selskab. Math. fys. Medd.*, **15**, No. 13, 4 (1937).

A few drops of the deuterium oxide is run from the funnel into the flask containing a two to three mole excess of benzoyl chloride (reagent grade). The flask is gently heated until deuterium chloride is evolved at a satisfactory rate, and the temperature is maintained at this level until all of the deuterium oxide has been added and the evolution of gas has noticeably slackened. The temperature is then slowly raised to the boiling point of the benzoyl chloride and maintained there until gas is no longer produced.

At the end of the reaction, a slow stream of dry air is passed into the system through the dropping funnel (the refluxing of the reaction mixture is not interrupted) to force the last traces of deuterium chloride to the outlet. At all times the evolution of deuterium chloride is smooth, easily controlled (the addition of a few chips of porous plate to the reaction flask is advisable), and may be halted simply by removing the source of heat.

The details of one test preparation will be given to illustrate the yields and degree of purity which may be expected.

Five ml. (0.550 equiv.) of deuterium oxide (99.6%) were treated with an excess (*ca.* 1.5 moles) of benzoyl chloride. The deuterium chloride obtained was dissolved in distilled water (contained in a 250-ml. volumetric flask), the solution in the flask diluted to the mark, and samples removed for analysis. Total acidity found was 0.528 equiv. (average of three determinations: 0.526, 0.527, 0.531), representing a yield of 96% of the theoretical. The solution was analyzed volumetrically for chloride ion by the Volhard method; found: 0.529 equiv. (average of three determinations: 0.528, 0.530, 0.530). The deuterium content was determined by the temperature float method on a portion of the solution after the acid had been carefully neutralized with barium oxide and the water distilled; found: 0.528 equiv. of deuterium (average of two determinations: 0.530, 0.526). It is evident that, within the accuracy of the experiment, a nearly quantitative yield[7] of pure deuterium chloride had been obtained

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Summary

Deuterium chloride may be prepared conveniently by the action of benzoyl chloride on deuterium oxide at elevated temperatures. The product is analytically pure and the yields (based on the available deuterium) are practically quantitative.

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[7] In three preliminary experiments in which 9 to 18 g. of water (1.0 to 2.0 equiv.) were transformed into hydrogen chloride by this method. the yields obtained were 98.5, 100, 99%.

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NOTES

Physical Constants of Methyl Isopropenyl Ketone

BY JOSEPH H. BRANT

The literature dealing with methyl isopropenyl ketone[1-8] shows a considerable variance with respect to the physical constants of this ketone. Two methods of preparation have been described in the recent literature. The liquid phase synthesis from methyl ethyl ketone and formalin has been studied extensively by Morgan and coworkers[2,3] and also by Rutovskii and coworkers.[4,5,6] A vapor phase synthesis has been described by Brant and Hasche[7] in which the ketone is produced in one step starting with methyl ethyl ketone and formalin or paraformaldehyde.

More recently Marvel, Riddle and Corner[8] reported the boiling point of methyl isopropenyl ketone as 45–46° at 40 mm. It would appear that this value is considerably too high.

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[1] Beilstein IV, Vol. I, p. 733, Supp., 381.

[2] Morgan, Megson and Pepper, *Chemistry and Industry*, **57**, 390 (1938).

[3] Morgan, Megson and Pepper, *ibid.*, **57**, 885 (1938).

[4] Rutovskii and Yakobson, *J. Applied Chem.*, (U. S. S. R.), **14**, 528 (1941).

[5] Rutovskii and Dmitrieva, *ibid.*, **14**, 535 (1941).

[6] Rutovskii and Goncharov, *ibid.*, **14**, 542 (1941).

[7] Brant and Hasche, U. S. Patent 2,245,567.

[8] Marvel, Riddle and Corner, THIS JOURNAL, **64**, 92 (1942).