4-(Trichloromethyl)phthalic Anhydride

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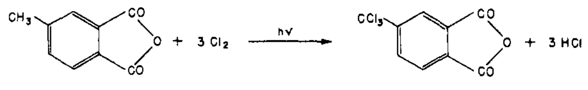
THE synthesis of the new compound, 4-(trichloromethyl)-phthalic anhydride (II), by light-catalyzed chlorination of 4-methylphthalic anhydride (I) in the molten state is reported.



I II

Compound I was prepared by the bromination of 4-methyl-1,2,3,6-tetrahydrophthalic anhydride and dehydrobromination of the resulting brominated compound in accordance with a procedure reported previously (*1*).

EXPERIMENTAL

Chlorine gas was introduced at a rate of 11.8 grams per minute into molten I (823.0 grams; 5.07 moles) over a period of about 38 hours, while the temperature was increased gradually from 100° C. to 230° C. The reaction mixture was irradiated with a 22-watt, cool white fluorescent lamp. Fractional distillation of the light-yellow, viscous liquid gave 1121 grams (83.4% yield) of 4-(trichloromethyl)phthalic anhydride, b.p. 162–163° C. (1.8 mm.), n_D^{25} 1.592. Anal. Calcd. for $C_9H_3Cl_3O_3$: C, 40.71; H, 1.13; Cl, 40.15. Found: C, 40.49; H, 1.33; Cl, 39.60. Infrared spectrum (Perkin Elmer 221, liquid film): 3090 cm.$^{-1}$ (m., C—H stretching); 1855 cm.$^{-1}$ (s., C=O stretching); 1785 cm.$^{-1}$ (s., C=O stretching); 1620 cm.$^{-1}$ (m., aromatic C=C stretching); 1262 cm.$^{-1}$ (s., C—O—C stretching); 950 cm.$^{-1}$ (s., C—H bending); 895 cm.$^{-1}$ (s., C—H bending); 770 cm.$^{-1}$ (s., C—Cl stretching); 675 cm.$^{-1}$ (m., unassigned).

LITERATURE CITED

(1) Newman, M.S., McCleary, C.D., *J. Am. Chem. Soc.* **63**, 1542 (1941).

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Determination of the Standard Heat of Formation of 3,3′-Thiodipropionitrile

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A thermochemical study of the reaction between acrylonitrile and hydrogen sulfide in the presence of ammonia catalyst has been made. The primary reaction under the conditions investigated was the formation of 3,3′-thiodipropionitrile (TDPN). The heat of reaction was used in conjunction with the already known heats of formation of acrylonitrile, ammonium sulfide, and ammonia to derive the heat of formation of TDPN.

THE determination of the standard heat of formation of 3,3′-thiodipropionitrile (TDPN) in this investigation was carried out in a simple glass Dewar-vessel calorimeter. This apparatus was easily constructed, inexpensive, and easy to operate, yet it was calorimetrically reliable. The reaction occurring in the calorimeter was assumed to follow Equation 1.

$$2CH_2{:}CHCN\ (liq.) + (NH_4)_2S\ (aq.) = S(CH_2CH_2CN)_2\ (liq.) + 2NH_3\ (aq.) \quad (1)$$

The thermochemistry of this reaction provides a route to the heat of formation of TDPN since the heats of formation of all other components in the reaction were known.

EXPERIMENTAL

Chemicals. The acrylonitrile (American Cyanamid Co.) was refined in the laboratory by distillation to remove stabilizing agents. The ammonium sulfide solution was prepared by bubbling hydrogen sulfide gas through concentrated ammonium hydroxide solution. The TDPN was this laboratory's purified product, m.p. 28.6° C., purity estimated to be over 99%.

Apparatus. The equipment was similar to that described by Daniels, Mathews, and Williams (*3*) except that the calorimeter had a capacity of one liter and a graduated funnel was used for introducing samples.

Procedure. In a typical run, the Dewar-flask was charged with 1000 grams of solution of the following composition by weight: acrylonitrile, 5%; TDPN, 30%; and distilled water, 65%. The initial temperature of the system was adjusted to about 30° C. and was allowed time to achieve steady state thermally, with stirrer in motion. The tests were carried out by adding, through the dropping funnel, to the contents of the Dewar-vessel, 10-gram portions of ammonium sulfide solution containing about 20% hydrogen sulfide (the actual concentration was predetermined by analysis). The ammonia in the ammonium sulfide solution served as a catalyst of the cyanoethylation reaction. An initial concentration of ammonia catalyst of about 0.2% was used. The temperature rise of the system caused by the heat of reaction was evaluated from a time-temperature plot. The total temperature rise during each test was approximately 2.5° C. The reaction went to completion in a matter of minutes. Corrections were made to the enthalpies of the initial reactants and final products to refer to the reaction at 25° C. This was done by determining the electrical energy equivalent of the calorimeter and contents

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