4 g. (94%) of yellow-brown prisms, m.p. 136.5–137.5°, were obtained; soluble in ether, ethanol, acetone, chloroform benzene and dilute aqueous acid, slightly soluble in petroleum ether, insoluble in water. After three successive crystallizations from methanol the m.p. was raised to 138.5–139.5°; formed no picrate. Wool was dyed to a beautiful lemon-yellow color in a hot solution of IV in the presence of sulfuric acid.

Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.36; H, 5.88; N, 16.33. Found: C, 65.38; H, 5.91; N, 16.34.

(b) From II.—Fourteen grams (0.067 mole) of II was refluxed in 160 ml. (1.75 moles) of aniline for 8 hours. The excess aniline was steam distilled and the residue treated as in (a); yield 12 g. (70%); no depression of m.p. when mixed with preparation from (a).

2-Acetylamino-5-dimethylaminodiphenylamine.—Fifteen grams (0.058 mole) of IV was suspended in a mixture of 150 ml. of ethyl acetate, 25 ml. (0.264 mole) of acetic anhydride and 250 mg. of platinum oxide. The mixture was hydrogenated at room temperature at 40 lb. until the theoretical uptake of hydrogen was reached (about 4 hours). The excess hydrogen was vented, 200 ml. of petroleum ether added and the mixture allowed to stand for a half-hour. Two crystallizations from benzene–petroleum ether gave long colorless needles, m.p. 161–162°. Soluble in ether, ethanol, acetone, chloroform and benzene, slightly soluble in water, insoluble in petroleum ether.

Anal. Calcd. for $C_{16}H_{19}N_3O$: C, 71.40; H, 7.07; N, 15.61. Found: C, 71.38; H, 6.95; N, 15.47.

2-(2-Hydroxybenzal)-imino-5-dimethylaminodiphenylamine.—Two grams of IV was hydrogenated in 220 ml. of absolute ethanol over 100 mg. of platinum oxide at room temperature under 50 lb. pressure for 3 hours. The solution was filtered rapidly under nitrogen, 2.2 g. of salicylaldehyde added and the mixture refluxed for 1 hour. The yellowish-gray solution was concentrated to 10 ml. and kept in the refrigerator overnight. The crystalline mass was filtered and yielded 0.66 g. (23%) of orange-yellow rhombic platelets, soluble in ether, acetone, petroleum ether, insoluble in water; after two recrystallizations from ethanol, the m.p. was 137.5–138.5°.

Anal. Calcd. for $C_{21}H_{21}N_3O$: C, 76.10; H, 6.39; N, 12.68. Found: C, 76.15; H, 6.61; N, 13.04.

Acknowledgment.—This investigation was supported in part by Grant C355 of the National Cancer Institute, Public Health Service and Institutional Grant 71 from the American Cancer Society.

McArdle Memorial Laboratory, Medical School
University of Wisconsin
Madison, Wisconsin

The Decomposition of Trichloroacetic Acid Alone and in Glycerol

By Louis Watts Clark[1]

Received November 30, 1954

Kinetic studies have been made of the decomposition of trichloroacetic acid or its salts in various solvents, *e.g.*, water and aniline,[2] dioxane–water,[3] ethanol–water[4] and formamide–water.[5] These studies have indicated that the reaction is a unimolecular decomposition of the trichloroacetate ion.

To the list of solvents already reported[2] which promote the decomposition of trichloroacetic acid may be added glycerol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, 1,4-butanediol, 2-methylpentanediol-2,4 and 2-ethylhexanediol-1,3. The ability of these solvents to promote the decomposition of trichloroacetic acid falls in line with the proposed mechanism of the anion decomposition, since the acid would be expected to be somewhat ionized in polyhydric alcohols.

It is also of interest, and not previously reported, that trichloroacetic acid itself decomposes at a measurable rate at about 160° when a sufficient quantity of the acid (at least one mole) is used.

The present paper describes the results of kinetic studies which have been carried out on the decomposition of trichloroacetic acid in glycerol as well as in the molten state by measuring the volume of carbon dioxide evolved with time. Further investigations in this field are in progress.

Experimental

Reagents.—Trichloroacetic acid, analytical reagent grade, and glycerol, analytical reagent grade, 95% assay, were used in these experiments.

Apparatus.—The experiments described in this paper were carried out in an apparatus similar to that used by the author in studying the decomposition of formic acid.[6]

Decomposition of Trichloroacetic Acid in Glycerol.—A 0.2916-g. sample of trichloroacetic acid (sufficient to yield 40.0 ml. of carbon dioxide at S.T.P.) was weighed into a paper-thin glass capsule. The capsule was supported in the lower neck of the reflux condenser by means of a wire which was bent into a loop at the lower end. The lower end of the condenser was attached by standard taper joint to one neck of a 2-neck 200-ml. round-bottom Pyrex brand flask immersed in the constant temperature oil-bath. The upper end of the wire projected beyond the top of the condenser after piercing a rubber policeman sealing the upper end of a small T-tube attached to the top of the condenser. The other end of the T-tube made connection with the water jacketed buret. A slight twist of the wire by the operator at the proper moment sufficed to dislodge the capsule from its resting place and permit it to drop into the reaction flask. The capsule was then immediately crushed and its contents mixed with the solvent by the mercury sealed stirrer. The course of the reaction was followed by measuring the volume of gas forced over into the buret by the evolution of carbon dioxide in the reaction flask.

In every experiment the total volume of gas collected was the stoichiometric amount within the limits of error of the measurements and the ideal gas law. At 109.0°, for example, the final observed volume of carbon dioxide, corrected to S.T.P., was 40.5 ml.; at 110.1°, 39.1 ml.; at 112.5°, 40.3 ml.; at 112.6°, 40.8 ml., and at 114.9°, 40.7 ml.

Decomposition of Trichloroacetic Acid Alone.—One mole (163.8 g.) of trichloroacetic acid was weighed into the dry reaction flask which was placed in the thermostat oil-bath at constant temperature. The acid quickly melted, and the mercury sealed stirrer was started. After temperature equilibrium was established carbon dioxide was evolved at a steady rate, and the volume of gas produced with time was carefully checked at each temperature. Determinations at each temperature were continued for periods of approximately one hour. The amount of trichloroacetic acid which decomposed during this period of time was negligible in comparison with the amount present, and hence the rate of decomposition was constant with time.

Results and Discussion

Decomposition of Trichloroacetic Acid in Glycerol.—Typical data for one run are given in Table I. The specific reaction velocity values, shown in the last column of the table, were calculated from the data on the basis of a first-order reaction.

The average value of k in sec.$^{-1}$ at 109.0° was 0.00153; at 110.1°, 0.00201; at 112.5°, 0.00271; and at 114.9°, 0.00360. For the temperature range 109.0–114.9°, E was found to be 41,700 cal.

---

[1] Saint Joseph College, Emmitsburg, Md.

[2] F. H. Verhoek, This Journal, **56**, 571 (1934).

[3] E. J. Salmi and R. Korte, *Ann. Acad. Sci. Fennicae*, **A54**, No. 10 (1940).

[4] G. A. Hall, Jr., and F. H. Verhoek, This Journal, **69**, 613 (1947).

[5] C. N. Cochran and F. H. Verhoek, *ibid.*, **69**, 2987 (1947).

[6] H. N. Barham and L. W. Clark, *ibid.*, **73**, 4638 (1951).

TABLE I

DECOMPOSITION OF TRICHLOROACETIC ACID IN GLYCEROL. SPECIFIC REACTION VELOCITY CONSTANTS AT 110.1°

Time, sec.	Vol. CO_2 at S.T.P., ml.	Completion of reacn., %	Spec. reacn. velocity
180	11.6	29.0	0.00191
240	14.8	37.0	.00192
300	17.8	44.5	.00196
360	20.4	51.2	.00192
420	23.0	57.6	.00204
480	25.3	63.5	.00208
540	27.2	68.2	.00211
600	28.9	72.3	.00213

One run was made at 109.0° on a 50% by weight mixture of glycerol–water yielding a value of k of 0.00259 sec.$^{-1}$, or nearly twice the value in the case of the 95% glycerol run, a result consistent with the proposed mechanism.

Decomposition of Trichloroacetic Acid Alone.—The average volume of carbon dioxide at S.T.P. evolved per minute from one mole of trichloroacetic acid at 156.4° was 1.51 ml.; at 159.4°, 2.5 ml.; at 163.8°, 5.03 ml.; and at 166.6°, 8.37 ml. These results yield specific reaction velocity constants in sec.$^{-1}$ of 1.12×10^{-6}, 1.865×10^{-6}, 3.71×10^{-6} and 6.17×10^{-6}, respectively. For the temperature range involved E is 60,700 cal.

DEPARTMENT OF CHEMISTRY
PANHANDLE AGRICULTURAL AND MECHANICAL COLLEGE
GOODWELL, OKLAHOMA

Preparation of N-Substituted Hydrazines from Amines and Chloramine

BY L. H. DIAMOND AND L. F. AUDRIETH

RECEIVED FEBRUARY 14, 1955

We have shown in a recent publication[1] that the Raschig hydrazine synthesis may be modified to yield simple monoalkyl hydrazines. The interaction of chloramine with amines has now been shown to constitute a general preparative method as illustrated by the conversion of *n*-hexylamine and cyclohexylamine into the corresponding hydrazines, of allylamine to allylhydrazine, ethanolamine to β-hydroxyethylhydrazine, ethylenediamine to β-aminoethylhydrazine, and morpholine to N-aminomorpholine. Attempts to prepare hydrazinoacetic acid from glycine by this method were unsuccessful.

Experimental

The experimental conditions were similar to those employed previously for the preparation of the simpler monosubstituted aliphatic hydrazines.[1] The cold reaction mixture, consisting of an aqueous chloramine solution prepared from hypochlorite and ammonia containing 0.04 mole of NH_2Cl in 250 ml., 0.25 g. of gelatin and the desired amine (mole ratio NH_2Cl:amine = 1:8), was allowed to warm to room temperature over a period of one hour and then heated on a steam-bath for an additional 10 to 30 minutes to ensure completion of the reaction. An aliquot of the reaction mixture then was analyzed by the iodate procedure to determine the percentage conversion of the amine into the corresponding hydrazine. The N-substituted hydrazines were isolated as salts either by concentration of the reaction mixture for the removal of the excess amine and water, followed by recovery of an aqueous fraction which was converted to the hydrochloride or the sulfate (method A), or by neutralization of the reaction mixture with acetic acid followed by treatment with either benzaldehyde or salicylaldehyde for conversion to the azine, extraction of the latter with ether and treatment of the ether solution with aqueous oxalic acid followed by distillation for the removal of the aldehyde and ether and then subsequent concentration to crystallization, after which the oxalate was purified for analysis (method B).

***n*-Hexylhydrazine Hydrogen Oxalate.**—Method B: from 32.0 g. of *n*-hexylamine; 57% yield. Most of the N-substituted hydrazine was found to separate from solution along with the excess amine as a non-aqueous water-insoluble layer upon cooling. The reaction mixture was neutralized with 200 ml. of glacial acetic acid, filtered, and the filtrate condensed with 8 g. (0.069 mole) of benzaldehyde and extracted with three 75-ml. portions of ether. The ether extracts were added to 7.5 g. of oxalic acid dihydrate dissolved in 100 ml. of water. The suspension was steam distilled to remove benzaldehyde, and *n*-hexylhydrazine hydrogen oxalate was obtained by concentration of the residue. The material was recrystallized from ethanol, m.p. 178°.

Anal. Calcd. for $C_8H_{18}O_4N_2$: C, 46.59; H, 8.80; N, 13.59. Found: C, 46.55; H, 8.91; N, 13.77.

Cyclohexylhydrazine Sulfate.—Method A: from 30.2 g. of cyclohexylamine; 60% yield. The product plus the excess of the amine formed a separate liquid phase. The reaction mixture was fractionated to remove the amine and the aqueous hydrazine fraction treated with an excess of sulfuric acid. Cyclohexylhydrazine hydrogen sulfate was obtained upon evaporation and recrystallized from methanol with the addition of ether, m.p. 117°.

Anal. Calcd. for $C_6H_{16}O_4N_2S$: C, 33.95; H, 7.60; N, 13.20. Found: C, 34.16; H, 7.80; N, 13.16.

Allylhydrazine dihydrochloride: from 18.9 g. of allylamine; 52% yield by analysis. The product was isolated by method A as the dihydrochloride, m.p. 133–35° (lit. 134–140°[2]).

β-Hydroxyethylhydrazine Hydrogen Oxalate.—From 19 g. of ethanolamine; 58% yield. The hydrogen oxalate, m.p. 106°,[3] was isolated from the reaction mixture using method B.

Anal. Calcd. for $C_4H_{10}O_5N_2$: C, 28.92; H, 6.07; N, 16.86. Found: C, 28.62; H, 6.19; N, 16.60.

β-Aminoethylhydrazine Dioxalate.—From 20 g. of ethylenediamine; 75% yield. The dioxalate, m.p. 206°,[3] was isolated from the reaction mixture by method B.

Anal. Calcd. for $C_6H_{13}O_8N_3$: C, 28.24; H, 5.14; N, 16.47. Found: C, 28.25; H, 5.11; N, 16.70.

N-Aminomorpholine: from 28 g. of morpholine. A yellow oil remained behind with the residual material upon distillation. The product was extracted with ether and then fractionated, that portion boiling at 162–165° being converted to the hydrochloride. N-Aminomorpholine hydrochloride was found to melt at 167° (lit. 164°[4]).

Anal. Calcd. for $C_4H_{11}N_2OCl$: C, 34.65; H, 8.00; N, 20.20. Found: C, 35.08; H, 8.03; N, 19.89.

Acknowledgment.—This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

---

[1] L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

(2) S. Gabriel, *Ber.*, **47**, 3028 (1914).

(3) G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

(4) L. Knorr and H. W. Brownsdon, *Ber.*, **35**, 4474 (1902).

NOYES LABORATORY OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Reductive Cleavage of Esters and Lactones by Grignard Reagents

BY REYNOLD C. FUSON AND DONALD E. BRASURE[1]

RECEIVED JANUARY 29, 1955

Carboxylate ion displacement studies in the dimesitylmethyl ester series with Grignard reagents

---

(1) Socony-Vacuum Fellow, 1952–1953.