ture, 220.68 ± 0.1°. An examination of the boiling points and their differences above and below this temperature will show that the limit of 0.1° is justified. Calculation of the crossover point by means of the vapor pressure ratio equation yields a much less precise temperature of 221.04°. The pressure corresponding to the crossover temperature as calculated from the steam tables is 340.9 p.s.i.a.

Critical Constants.—Riesenfeld and Chang[6] reported a value of 371.5° for the critical temperature of D_2O which is 0.6° higher than the value 370.9 ± 0.1° determined in this work. In Fig. 1, there is a plot of vapor pressure data near the critical region for both D_2O and H_2O. It should be stated that the points marked A were measured with considerable difficulty, consequently their values are less precise. The curve representing the pressure and temperature relationship of H_2O is well defined by several points to show that the slope increases rapidly and approaches infinity at the accepted critical temperature[8] of 374.11 ± 0.1°. According to the phase relationship this should be true, since the liquid–vapor state no longer exists as such, the heat of evaporation has diminished toward zero, and any change in pressure does not cause a corresponding change in temperature. A similar curve was observed for D_2O in which dp/dt approaches infinity at 370.9°. The measurement of the critical temperature by the sealed quartz tube method yielded a value of 370.8 ± 0.1°; therefore it was concluded that the critical temperature of D_2O is 370.9 ± 0.1°. From an enlarged plot of Fig. 1, one may estimate the critical pressure of D_2O to be 3170 ± 5 p.s.i.a. This value is considerably less than the 3213 p.s.i.a. calculated by Reisenfeld and Chang from the pressure of H_2O and critical temperature of D_2O.

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TEXAS CITY, TEXAS

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Preparation of Some N-Disubstituted Hydrazines by Reaction of Chloramine with Secondary Amines

BY R. A. ROWE AND L. F. AUDRIETH

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The chloramine–amine reaction has been extended to include preparation of some typical N-dialkylhydrazines, R_2NNH_2 (where R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9). Use of an excess of ammonia in the preparation of chloramine from hypochlorite markedly improves dialkylhydrazine yields.

The reaction for the preparation of N-monosubstituted hydrazines from chloramine and the corresponding primary amines[1,2] has been extended to include some typical N-dialkylhydrazines, R_2NNH_2 (where R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9).

Chloramine solutions had previously been prepared by allowing hypochlorite and ammonia to react in equimolecular amounts. The analyzed chloramine content of such solutions usually varied between 50 to 60% of theory and this figure was employed in calculating yields of the alkyl hydrazines. It has been shown recently[3] that the available chloramine content of such solutions approaches that demanded theoretically when a 3/1 ammonia–hypochlorite mole ratio is employed. Since the amine–chloramine reactions take place much more rapidly than the ammonia–chloramine reaction, no difficulties were experienced in effecting the synthesis of the N-disubstituted hydrazines. Markedly greater yields of typical N-dialkyl hydrazines were obtained by employing an excess of ammonia in the preparation of chloramine.

Experimental

Analytical Methods.—Sodium hypochlorite solutions were prepared by the method of Coleman and Johnson.[4] The hypochlorite content was determined iodometrically. The excess sodium hydroxide in the hypochlorite solutions was determined by pH titration with standard hydrochloric acid to an equivalence point in the range of pH 10.2–10.4. An iodometric procedure was employed for chloramine.

The iodometric procedure[5] used for hydrazine proved to be adaptable to N-disubstituted hydrazines. Oxidation to the tetrazene occurs in solutions, maintained at a pH of 7–7.4, in accordance with the equation

$$2R_2NNH_2 + 2I_2 = R_2N{\cdot}N_2{\cdot}NR_2 + 4HI$$

Titration is carried out in a nitrogen atmosphere. The iodine solution is added rapidly to just about 1 ml. short of the approximate end-point at which time the starch solution is added. The drop which causes the solution to turn completely purple is considered to be the best end-point, even though the indicator fades rapidly thereafter.

Effect of the Ammonia/Hydrochlorite Ratio on the Yields of N,N-Disubstituted Hydrazines.—Chloramine solutions were prepared using 1:1, 2:1 and 3:1 mole ratios of ammonia to hypochlorite. Both reagents were first precooled to 0°. A 100-ml. quantity of the appropriate ammonia solution was then added to 50 ml. of 1 M sodium hypochlorite (0.44 M in sodium hydroxide). The resulting chloramine solutions were allowed to stand at 0° for 90 minutes and then treated with 50 ml. of a 4 M solution of the amine (diethylamine or piperidine).[6] After 30 minutes at 0°, the reaction mixtures were allowed to warm to room temperature before being analyzed iodometrically for dialkyl hydrazine content.

For mole ratios of ammonia to hypochlorite = 1, 2 and 3, the yields of diethylhydrazine were found to be 48, 57 and 63%, respectively. Percentage yields of N-aminopiperidine under similar conditions were found to be 28, 42 and

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

[2] L. H. Diamond and L. F. Audrieth, *ibid.*, **77**, 3131 (1955).

[3] L. F. Audrieth and R. A. Rowe, *ibid.*, **77**, 4726 (1955).

[4] G. H. Coleman and H. L. Johnson, *Inorg. Syntheses*, I, 60 (1939).

[5] R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

[6] Preliminary experiments had shown that the dialkyl hydrazine yields level off at an amine/NH_2Cl mole ratio of about 4:1.

51%. It is evident, therefore, that the yields of N-disubstituted hydrazines, based upon the amount of hypochlorite used, rise markedly as the ammonia/hypochlorite ratio required to produce chloramine is increased beyond stoichiometric quantities to a 3/1 reaction mixture.

Preparation of Some N-Dialkylhydrazines.—For the preparation of larger quantities of unsymmetrically disubstituted hydrazines the following procedure was employed. An ice-cold solution of chloramine, prepared by adding 250 ml. (0.25 mole) of a cold 1 *M* sodium hypochlorite solution to 750 ml. of aqueous ammonia (0.75 mole), was allowed to react with one mole of the appropriate amine (mole ratio, amine to hypochlorite = 4:1). All reaction mixtures were permitted to rise to room temperature over a period of four hours before aliquots were analyzed iodometrically for the dialkyl hydrazine content and then further treated to effect isolation of the desired hydrazine. The water soluble amines, dimethylamine and diethylamine, react quickly with chloramine in the cold. With water-insoluble amines it was found desirable to agitate the reaction mixture vigorously for a period of 30 minutes after the solutions had reached room temperature. The water-soluble hydrazines were recovered by fractional distillation (method A). The less soluble dialkyl hydrazines were extracted from the reaction mixtures with petroleum ether (method B). The various dialkyl hydrazines were converted into the hydrogen oxalates for characterization and analysis. Given yields for typical experiments represent grams of the purified hydrogen oxalates actually recovered.

N-Dimethylhydrazine hydrogen oxalate, $(CH_3)_2NNH_2 \cdot H_2C_2O_4$: method A, 20 g. (53.2%), m.p. 142° (lit. 142°[7]).

N-Diethylhydrazine hydrogen oxalate, $(C_2H_5)_2NNH_2 \cdot H_2C_2O_4$: method A, 18.2 g. (40.8%), m.p. 138°.

Anal. Calcd. for $C_6H_{14}N_2O_4$: C, 40.49; H, 7.91; N, 15.72. Found: C, 40.85; H, 8.03; N, 15.50.

N-Di-*n*-propylhydrazine hydrogen oxalate $(C_3H_7)_2NNH_2 \cdot H_2C_2O_4$: method B, 11.8 g. (40%), m.p. 168°.

Anal. Calcd. for $C_8H_{18}N_2O_4$: C, 46.44; H, 8.79; N, 13.56. Found: C, 46.31; H, 8.86; N, 13.11.

N-Di-*n*-butylhydrazine hydrogen oxalate, $(C_4H_9)_2NNH_2 \cdot H_2C_2O_4$: method B, 15.0 g. (41.7%), m.p. 170°.

Anal. Calcd. for $C_{10}H_{22}N_2O_4$: C, 51.25; H, 9.49; N, 11.96. Found: C, 51.50; H, 9.09; N, 12.08.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Intramolecular Carbon Isotope Effect in the Decarboxylation of the Mono-anion of Malonic Acid in Quinoline Solution

BY PETER E. YANKWICH AND H. S. WEBER

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The intramolecular carbon isotope effect in the decarboxylation of the mono-anion of malonic acid in quinoline solution has been investigated over the temperature range 79–138°; temperature dependence of the oxygen isotope constitution of product carbon dioxide suggests that the C–O linkages are involved directly in the process of activation. The carbon isotope effect results are compared with those previously obtained for the intermolecular case in terms of the simple bond-rupture model suggested by Bigeleisen. This comparison yields reasonable values for the equilibrium constant for isotope discrimination in anion formation and the ratio of the isotopic constants for complex formation involving the solvent.

Introduction

In a recent paper[1] we presented the results of experiments designed to measure over the temperature range 67.5 to 119° the intermolecular isotope effect in the decarboxylation of the mono-anion of malonic acid in quinoline solution. From the temperature dependence of that isotope effect, and the influences of solvent and added 1-butylpiperidine on the rate of decarboxylation and the position of the carbonyl absorption band, it was inferred that there were, impressed upon that due to bond rupture, isotope effects originating in equilibria between solvent and solute and/or in non-random distribution of C^{13} among the various anionic species.

In the investigation to be reported here, work with the malonic acid–quinoline–butylpiperidine system was extended to the determination of the intramolecular isotope effect over the temperature range 79–138°; the results are compared with the intermolecular isotope effect in the common temperature interval.

Experimental

No basic change was made in the materials, apparatus, general procedure, isotope analyses or calculation methods employed in previous studies[1-3]; the minor modifications required in the present work are described below.

Procedure.—In a typical experiment 45 ml. of quinoline and 0.4 ml. (2.3 mmoles) of 1-butylpiperidine were mixed and brought to the desired temperature, as was 104 mg. (1 mmole) of malonic acid. The acid was then combined with the mixed solvent and effluent gas collection started; the reaction time ranged from 2.5 hours at 138° to 77 hours at 79°. Because of these very long collection times, even when the sweep rate of preheated carbon dioxide-free helium was reduced to 10–20 cc./min. it was necessary to make even more thorough the purification of the product carbon dioxide. To this end, the samples of product gas were subjected to three distillations: the first from a Dry Ice–alcohol bath at −78° to a trap cooled in liquid nitrogen; the second and third from that trap held between −155 and −145° to one cooled in liquid nitrogen. Quantitative transfers of carbon dioxide were assured by continuous monitoring of the ambient pressure in the distillation apparatus; occasional checks were made by means of accurate quantity determinations before and after purification.

Calculations.—Since we do not *know* from which end of the anion the carbon dioxide product comes, it will be convenient to adopt a variant of the notation employed in the previous paper[1]; having reference only to the carbon skeletons of the molecules, we write

$$C^{12}—C^{12}—C^{12} \xrightarrow{k_1} C^{12} + C^{12}—C^{12} \quad (1)$$

$$C^{12}—C^{13}—C^{12} \xrightarrow{k_2} C^{12} + C^{13}—C^{12} \quad (2)$$

$$C^{13}—C^{12}—C^{12} \xrightarrow{k_3} C^{13} + C^{12}—C^{12} \quad (3)$$

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