N_2O_3 show a characteristic blue color with absorption over a narrow range at 6800 Å., the N_2O_3 group must absorb the energy. The N_2O_3 is now completely removed as in Step IIa or shifted in position as in Step IIb, forming an isomer designated here for convenience as the delta modification. Step IIb may possibly involve the removal of N_2O_3 as in Step IIa and then subsequent rearrangement and recombination. This isomerization allows the formation of the bimolecular compound as in Step III. The final Step IV yields nitrogen, some isomeric form of caryophyllene and the two nitrosates containing the N_2O_4 and N_2O_5 groups. The direct formation of nitrosates may account for the photochemical effect of oxygen in accelerating the photolysis as discussed previously.

The intensity of the light was changed four-fold without affecting the quantum yield as shown in Table I. The straight line obtained in Fig. 2 shows that the quantum yield was not affected by a change in concentration from a 0.0152 to 0.0009 molar.

The mechanism presented, while not definitely proved, agrees well with the physical data based on quantum yields for a product as well as for the disappearance of the original molecule. Any later mechanism founded on new chemical facts should be subjected to this test. It is suggested that such a procedure may be helpful in many problems involving complicated molecules.

It was hoped that a study of the simpler amylene nitrosite would yield further information on this problem. Preliminary experiments showed that the quantum yield is greater and that the products contain more nitrogen oxides.

The author wishes to express his gratitude for the helpful advice of Professor Farrington Daniels, throughout the course of this work.

Summary

1. The photolysis of β-caryophyllene nitrosite in red light has been measured quantitatively with a monochromator.
2. The gaseous products have been analyzed.
3. The quantum yield for nitrogen liberated is 0.38 molecule per quantum.
4. An improved method is presented for determining quantum yields by the decrease in the absorption of light.
5. The quantum yield for the disappearance of the nitrosite is 1.37 molecules per quantum.
6. Oxygen has been shown to affect the reaction.
7. A reaction mechanism has been proposed. The value of photochemical data in studying the reaction of complicated molecules is illustrated.

MADISON, WISCONSIN RECEIVED JUNE 15, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OREGON STATE COLLEGE]

Studies on Hydrazine: Transition Points and Dissociation Pressures of Hydrated Hydrazonium Salts

BY B. E. CHRISTENSEN AND E. C. GILBERT

Only a small number of hydrazonium salts are known to occur in the form of hydrates. The existence and constitution of several of these have been established by the authors.[1]

To this list should now be added a hydrate of the dihydrobromide. As a preparation for work requiring the use of both hydrated and anhydrous salts, a study has been made of the dissociation pressures and conditions of stability of the more important hydrated forms, namely, the monoperchlorate, monosulfate,[2] dihydrobromide and picrate. The other common and useful salts of hydrazine are always obtained in the anhydrous form and give no indication of hydrate formation.

Experimental Part

Preparation of Salts.—The picrate was prepared and analyzed as in previous work.[1a] It contained one-half molecule of water of hydration. The monosulfate when prepared by the method of Sommer and Wiese[3] was found to contain a considerable amount of hydrazonium carbonate as impurity. It was therefore prepared by reaction of the free base with sulfuric acid, followed by evaporation, and recrystallized from dilute alcohol. Analysis showed it to be the monohydrate.

Anal. Calcd. for $(N_2H_4)_2 \cdot H_2SO_4 \cdot H_2O$: N_2H_4, 35.58. Found: N_2H_4, 35.30, 35.30.

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[1] (a) Gilbert, *J. Phys. Chem.*, **33**, 1235 (1929); (b) THIS JOURNAL, **53**, 3956 (1931); (c) Gilbert and Huffman, *J. Phys. Chem.*, **36**, 2789 (1932); (d) Christensen and Gilbert, THIS JOURNAL, **56**, 393 (1934).

[2] So-named in this paper because the hydrazine functions as a monoacid base.

[3] Sommer and Wiese, *Z. anorg. Chem.*, **94**, 51 (1916).

The dihydrobromide was prepared likewise by reaction of excess hydrobromic acid on the base. Upon evaporation crystals of a dihydrate separated, were dried by pressing between filter paper and were allowed to stand open to the air for a short time. This salt was reported recently by us but its analysis has not previously been established.

Anal. Calcd. for $N_2H_4 \cdot 2HBr \cdot 2H_2O$: N_2H_4, 14.27. Found: N_2H_4, 14.04, 14.04.

The monoperchlorate proved to contain one-half molecule of water as previously reported.[1b] It was recrystallized from 80% alcohol and dried in the air.

Anal. Calcd. for $N_2H_4 \cdot HClO_4 \cdot {}^1/_2H_2O$: N_2H_4, 22.65. Found: N_2H_4, 22.54.

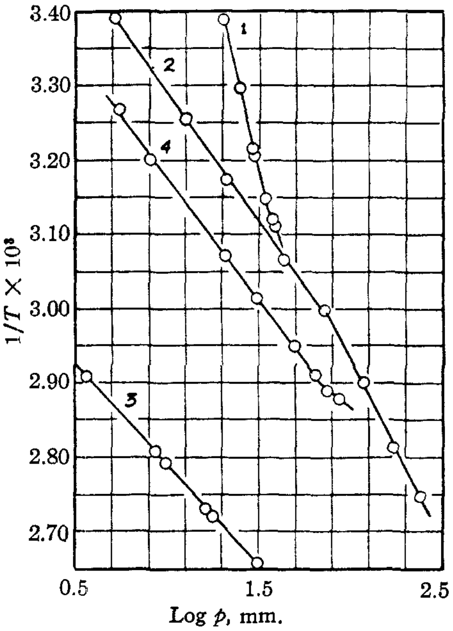

Fig. 1.—Dissociation pressures of hydrated hydrazonium salts: (1) monosulfate, (2) dibromide, (3) picrate, (4) monoperchlorate. (To avoid confusion Curve 4 has been lowered 0.1 unit so that a point where $1/T = 3.00$ in the figure should actually be located at 3.10.)

Determination of Dissociation Pressure.—Good sized samples of the salts were placed in an isoteniscope similar to that of Smith and Menzies.[4] The temperature was maintained constant in a well-stirred oil bath. Vapor pressures were read by means of a cathetometer and the temperature was read on a mercury thermometer which was calibrated against a platinum resistance thermometer. With the exception of the monosulfate, no difficulty was experienced in obtaining equilibrium and concordant results. The sulfate showed great sluggishness in crystallizing, even in the presence of solid, and qualitative results only could be obtained. In all cases, a considerable proportion of the water vapor was pumped off in order to ensure the presence of satisfactory amounts of the anhydrous phases.

The perchlorate, sulfate and dibromide hydrates all proved to have transition points, at which they decomposed into water and the anhydrous form. That for the sulfate has been reported previously, from solubility measurements.[3] The transition points for the perchlorate and dibromide were also obtained by direct observation of the time-temperature cooling curves, using a calibrated thermometer and large sized samples.

Results

The results are shown graphically in Fig. 1. The transition point for the perchlorate occurs at 60.5 ± 0.05° and that for the dibromide at 61.5 ± 0.05°. The picrate shows no break in the vapor pressure curve up to its melting point. It holds the water of hydration very tenaciously and begins to have an appreciable vapor pressure only at temperatures around 100°.

The transition point for the monosulfate agrees with that determined by Sommer and Wiese.[3]

Equations to fit the curves have been developed as follows

For $N_2H_4 \cdot HClO_4 \cdot 0.5H_2O$ up to 60.5°

$$\log p_{\text{mm.}} = -3047.6/T + 10.980$$

For $(N_2H_4) \cdot 2HBr \cdot 2H_2O$ up to 61.5°

$$\log p_{\text{mm.}} = -2857.1/T + 10.40$$

For $N_2H_4 \cdot C_6H_2(NO_2)_3OH \cdot 0.5H_2O$

$$\log p_{\text{mm.}} = -3681.1/T + 11.267$$

For $(N_2H_4)_2 \cdot H_2SO_4 \cdot H_2O$ up to 47.3°

$$\log p_{\text{mm.}} = -952.4/T + 4.53$$

Discussion

In their behavior as regards hydration, the hydrazonium salts are somewhat similar to sodium, in that the bromide contains two molecules of water, and the picrate and sulfate are also hydrated, whereas the corresponding potassium salts are not.

From the standpoint of the phase rule, each of the transition points observed should be a nonvariant point since there are present in equilibrium the hydrated solid, the anhydrous solid, solution and vapor.

From the slope of the pressure-temperature curves ΔH may be calculated for the dehydration of the salts. Changing the pressures to atmospheres also, the standard free energy change may be calculated with the following results: perchlorate

$$\Delta H = 13{,}954 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p^{1/2} = 1456 \text{ cal.}$$

Dibromide

$$\Delta H = 13{,}082 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p^2 = 5626 \text{ cal.}$$

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(4) Smith and Menzies, This Journal, **32**, 1427 (1910).

Picrate

$$\Delta H = 16{,}855 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p^{1/2} = 2705 \text{ cal.}$$

Sulfate

$$\Delta H = 4360 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p = 2131 \text{ cal.}$$

Summary

1. A new hydrate of hydrazonium dibromide is reported.

2. Dissociation pressures over a range of temperature are given for four of the five known hydrated hydrazonium salts, and transition points determined for two of them.

3. Calculations of the change in heat content and standard free energy change of hydration are made.

CORVALLIS, OREGON RECEIVED JUNE 20, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Chain Decomposition of Dimethyl Ether Photosensitized by Acetone

BY JOHN A. LEERMAKERS[1]

In a study of the photolysis of acetaldehyde at high temperatures[2] the author recently obtained experimental support of the chain theory of decomposition of organic compounds which was advanced by Rice and Herzfeld.[3] It was felt that this case might not be representative of the general type of decomposition which these authors consider, inasmuch as the course of the thermal decomposition of acetaldehyde[4] is best expressed by a kinetic equation which is not first order, while the other reactions discussed by them have been generally accepted as being unimolecular and are first order at high pressures.

The present investigation was undertaken in order to obtain some evidence as to the general validity of the chain mechanism by a study of several reactions whose thermal decompositions have been heretofore considered to be unimolecular. One such reaction discussed by Rice and Herzfeld is the decomposition of acetone.[5] Another reaction also considered by these authors is the decomposition of dimethyl ether. This latter reaction was studied by Hinshelwood and Askey.[6] Rice and Herzfeld postulate that the decompositions of acetone and dimethyl ether are chain reactions, and that methyl radicals are the chain carriers in each case.

It is possible to test this idea by introducing methyl radicals into these two compounds at temperatures below those at which the normal thermal decompositions proceed. In the present investigation methyl radicals were liberated in acetone by the photolysis of the vapor. In the case of dimethyl ether the radicals were produced in the reaction cell containing the ether by illuminating mixtures of ether and acetone with light of wave length 3130 Å. Dimethyl ether does not absorb light of this wave length, and the light absorbed by the acetone almost certainly results in the production of methyl radicals.[7] The studies of acetone alone under conditions which obtained when mixtures were investigated showed that the photochemical decomposition of acetone except for the primary act was not significant when ether was present. There was no appreciable dark reaction with either acetone or with mixtures.

Rates of decomposition of acetone alone and of dimethyl ether in mixtures of acetone and ether were studied over a range of pressures, temperatures and light intensities. The results show that the high temperature photolysis of acetone is not a chain reaction, that dimethyl ether can be caused to decompose by means of methyl radicals and that this decomposition results in the establishing of a chain. A few experiments were performed with mixtures of acetone and diethyl ether; these will be briefly discussed.

Experimental

Apparatus and Materials.—The apparatus has been described in the paper on the photolysis of acetaldehyde[2] and was unchanged except that the acetaldehyde was replaced by acetone, and a 2-liter flask containing dimethyl ether was sealed to the tubing leading to the reaction cell.

Dimethyl ether was prepared from methyl alcohol and

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[1] National Research Fellow in Chemistry.

[2] Leermakers, THIS JOURNAL, **56**, 1537 (1934).

[3] Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[4] Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933); Kassel, *J. Phys. Chem.*, **34**, 1166 (1930).

[5] Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **A111**, 245 (1926).

[6] Hinshelwood and Askey, *ibid.*, **A115**, 215 (1927).

[7] Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).