The Photolysis of β-Caryophyllene Nitrosite[1]

BY ROBERT M. HOFFMAN

It was observed in 1898 by Kremers[2] that β-caryophyllene nitrosite is decomposed in solution by red light with the liberation of nitrogen. It is also decomposed by heating to 80–110°.[3]

Experimental Procedure

The nitrosite was kindly given to us by Professor Edward Kremers of the Pharmacy Department of the University of Wisconsin. Its absorption spectrum has been studied by Mitchell.[4] He found that absorption in the visible region was confined to a narrow band with its head at about 6800 Å. This was confirmed in our laboratory.

Monochromatic light was obtained with a small Hilger monochromator. The light sources were quartz capillary lamps[5] of cadmium or zinc, and in some cases tungsten lamps. The thermopile-galvanometer system was calibrated with a standard lamp (C-132) furnished by the Bureau of Standards. A micro gas buret was attached directly to the reaction cell and thermostated at 28°. The volume of nitrogen liberated was measured to 0.001 cc. by weighing displaced mercury. Nitrobenzene was used as the solvent in these experiments on the evolution of gas, on account of its low vapor pressure.

In the optical method, a ten-volt tungsten lamp was used with a storage battery floated across the dynamo circuit to decrease variations in intensity. If there was any loss in the monochromatic nature of the light by the use of the tungsten lamp, it did not affect the quantum yields within the range of experimental error. Two identical cells were used, one filled with pure solvent as a reference. Toluene was used as the solvent in these experiments.

The dark reaction at room temperature was found to be negligible.

Experimental Results

Quantum Yields for Nitrogen.—These results are summarized in Table I where λ = wave length, t = time in minutes, v = volume of nitro-

gen liberated, and $\Phi^{N_2}_{C_{15}H_{24}N_2O_3}$ = yield of nitrogen molecules per quantum, using the notation of Holmes and Daniels[6] in which the experimentally measured product or reactant is designated by a superscript and the material which absorbs the quantum by a subscript.

TABLE I
QUANTUM YIELDS FOR NITROGEN

λ, Å.	Lamp	t, min.	v, cc.	$\Phi^{N_2}_{C_{15}H_{24}N_2O_3}$
6439	Cd arc	57.5	0.124	0.40
6439		58	.133	.39
6439		58.5	.103	.33
6362	Zn arc	65	.083	.36
6362		43.5	.053	.44
6800	Tungsten	360	.190	.35

Av. 0.38

Precautions were taken in these experiments to exclude oxygen, as its presence affected the quantum yield.

Quantum Yields by the Optical Method.— In measuring quantum yields by the bleaching out of the color, two difficulties must be overcome. First, Beer's law may not be strictly applicable to the absorbing system. Second, from the nature of the measurement, the light transmission must undergo a large change and this fact makes it difficult to determine the exact amount of energy absorbed. Neither $\log I_0/I$, which is proportional to the concentration, or the absorption $(1-I)/I_0$ will yield a straight line when plotted against time; therefore the value at the midpoint will not give the true average absorption. Furthermore, a value for the average absorption is useless if the intensity of the light source has changed during the experiment.

These difficulties were overcome in the following general method. The initial concentration is determined either by starting with a known amount, or more conveniently by reference to an experimentally determined curve relating concentration to light absorption as in Fig. 1 for β-caryophyllene nitrosite. The photolysis is continued until the final concentration is zero, as shown by the light transmission becoming 100%. The absorbed energy is calculated by averaging both the absorption and the light intensity over short in-

(1) Further details concerning this work may be obtained from a thesis prepared under the direction of Farrington Daniels and submitted by the author to the University of Wisconsin in 1933 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) E. Kremers, Pharm. Arch., 2, 273 (1899).

(3) Valenzuela and Daniels, Philippine J. Sci., 34, 187 (1927).

(4) Mitchell. J. Chem. Soc., 3238 (1928).

(5) Hoffman and Daniels, THIS JOURNAL, 54, 4225 (1932).

(6) Holmes and Daniels, ibid., 56, 633 (1934).

crements and summing these up. This is, in effect, a graphical integration of the total absorbed energy and is accurate whether the function is linear or not. For these data no dependence on Beer's law is necessary. Lastly, $\log I_0/I$ (or $-\log I/I_0$) is plotted not against time but against a function which will give a straight line when Beer's law holds.

I_0 = incident light
I = transmitted light
A = average absorption
t = time elapsed since start
Δt = length of increment in minutes
C_0 = initial concentration
C_t = concentration at time t
C_d = amount decomposed = $C_0 - C_t$
then $(\Delta t A I_0)$ = energy absorbed during increment
$\Sigma_0^t (\Delta t A I_0)$ = total energy absorbed during time t

The amount decomposed at time t is proportional to the total energy absorbed, therefore we may write

$$C_0 - C_t = K_1 \Sigma_0^t (\Delta t A I_0)$$

also $C_t = K_2 \log (I/I_0)_t$

then $C_0 - K_2 \log (I/I_0)_t = K_1 \Sigma_0^t (\Delta t A I_0)$

and $-\log (I/I_0) = (K_1/K_2) \Sigma_0^t (\Delta t A I_0) - C_0/K_2$

This equation yields a straight line by plotting $-\log (I/I_0)$ against $\Sigma_0^t (\Delta t A I_0)$. When $-\log (I/I_0)$ becomes zero, we have $K_1 \Sigma_0^t (\Delta t A I_0) = C_0$ and the Beer's law coefficient K_2 has disappeared. This equation is equivalent to the statement that "quantum yield times quanta absorbed equals

molecules decomposed" since K_1 is proportional to the quantum yield and contains the factor to convert the energy summation to total quanta. The quantum yields obtained by this method are shown in Table II.
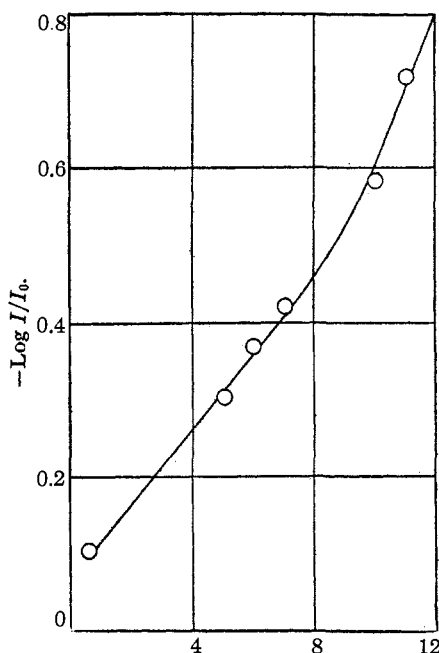
Grams of β-caryophyllene nitrosite per liter.

Fig. 1.—Concentration–light adsorption curve for β-caryophyllene nitrosite in toluene, cell depth 13.5 mm., $\lambda = 6800$ Å.

The first three experiments in Table II show, as before, that oxygen has a marked effect on the reaction. A limited number of data for the fourth experiment in Table II are given in Table III to illustrate the calculations and all the calculated points are graphed in Fig. 2.

In Table III I_0 and I are recorded simply as galvanometer deflections in centimeters. It will be

TABLE II
QUANTUM YIELDS BY THE OPTICAL METHOD

Gas present in cell	$\Phi \frac{C_{15}H_{24}N_2O_3}{C_{15}H_{24}N_2O_3}$
Air	2.8
Oxygen	2.9
Oxygen	2.9
Nitrogen	1.4
Nitrogen	1.4
Nitrous oxide	1.3

TABLE III
QUANTUM YIELD BY THE OPTICAL METHOD

Δt, min.	I_0, cm.	I, cm.	$1 - I/I_0$	I_0, av.	A, av.	$\Delta t A I_0$	$\Sigma_0^t (\Delta t A I_0)$	$-\log I/I_0$
0	95.9	35.3	0.638					0.4425
5	95.2	36.8	.618	95.6	0.628	300	300	.4179
2	95.0	37.1	.609	95.1	.614	117	417	.4078
			Eighteen increments omitted					
206	99.8	58.0	0.419	102.6	0.453	9560	30,251	0.2350
4	99.2	57.8	.417	99.5	.418	166	30,417	.2343
7	99.3	57.8	.417	99.2	.417	290	30,707	.2343
			Eighteen increments omitted					
130	80.1	75.2	0.061	80.0	0.065	675	73,927	0.0273
60	80.2	75.7	.056	80.1	.059	284	74,211	.0250
195	67.7	64.0	.055	73.7	.056	804	75,015	.0246

noted in Fig. 2 that the reaction is much faster at the beginning due to traces of oxygen which remain even after sweeping out the system with nitrogen. To exclude this effect, a later point is taken as the start of the reaction, namely, where $-\log I/I_0$ equals 0.359. From Fig. 1 this value gives an initial concentration of 0.0213 g. in about five cubic centimeters of solution. Figure 2 shows that, at completion, energy corresponding to 80,-000 galvanometer deflection-minutes has been absorbed. Subtracting the energy absorbed during
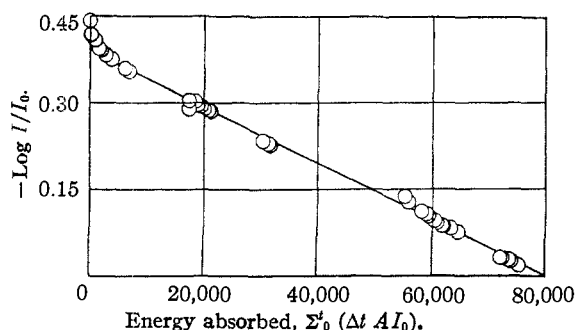

Fig. 2.—Quantum yield by the optical method.

the rapid initial oxygen reaction, one obtains $80,000 - 6250$ or 73,750 galvanometer deflection-minutes. The galvanometer factor (including a correction factor of 1.035 for reflection losses) is 4.57×10^{14} quanta/cm. deflection-minute. The molecular weight of the nitrosite is 280. The quantum yield is

$$\frac{(0.0213/280) \times 6.06 \times 10^{23}}{73,750 \times 4.57 \times 10^{14}} = 1.37$$

The Gaseous Products.—Kremers has shown that nitrogen is the main gaseous product of the photolysis of this nitrosite, although later Schreiner and Kremers[7] state that nitrogen oxides appear to be liberated also. Using a micro gas buret similar to the one described by Blacet and Leighton,[8] the gas was found to contain 13.9% (15.2 and 12.6) nitrogen trioxide and 86.1% (84.8 and 87.4) nitrogen. The nitrogen trioxide was absorbed with potassium hydroxide. As the N_2O_3 in the buret is largely dissociated into NO_2, N_2O_4, and NO, its undissociated volume was calculated from the equilibrium constants given by Verhoek and Daniels.[9] The volume of nitrogen gas per mole of nitrosite decomposed is 6478 cc. This value is the average of five determinations in which the mate-

(7) O. Schreiner, "The Sesquiterpenes," Pharm. Rev. Pub. Co., Milwaukee, 1904, p. 74.

(8) Blacet and Leighton, Ind. Eng. Chem., Anal. Ed., 3, 266 (1931).

(9) Verhoek and Daniels, THIS JOURNAL, 53, 1250 (1931).

rial was completely decomposed by direct light without using the monochromator. The nitrogen trioxide was removed either by freezing or by absorption in potassium hydroxide.
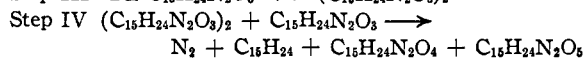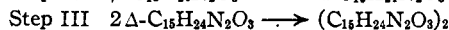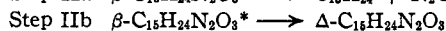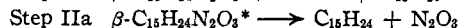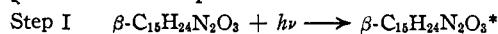
Theory

Reaction Mechanism.—The knowledge of β-caryophyllene nitrosite is at present so incomplete as to make difficult the choice of a reaction mechanism. It seems probable that the main, over-all reaction is an autoöxidation as follows

Reaction I

$3\beta\text{-}C_{15}H_{24}N_2O_3 + 2h\nu \longrightarrow N_2 + C_{15}H_{24} +$
$\qquad\qquad C_{15}H_{24}N_2O_4 + C_{15}H_{24}N_2O_5$
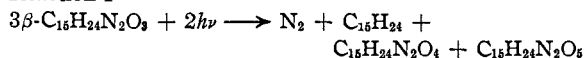
A termolecular collision involving two activated molecules and one normal molecule would be very improbable, therefore the following steps are postulated to explain Reaction I.[10]

Step I $\beta\text{-}C_{15}H_{24}N_2O_3 + h\nu \longrightarrow \beta\text{-}C_{15}H_{24}N_2O_3{}^*$
Step IIa $\beta\text{-}C_{15}H_{24}N_2O_3{}^* \longrightarrow C_{15}H_{24} + N_2O_3$
Step IIb $\beta\text{-}C_{15}H_{24}N_2O_3{}^* \longrightarrow \Delta\text{-}C_{15}H_{24}N_2O_3$
Step III $2\,\Delta\text{-}C_{15}H_{24}N_2O_3 \longrightarrow (C_{15}H_{24}N_2O_3)_2$
Step IV $(C_{15}H_{24}N_2O_3)_2 + C_{15}H_{24}N_2O_3 \longrightarrow$
$\qquad N_2 + C_{15}H_{24} + C_{15}H_{24}N_2O_4 + C_{15}H_{24}N_2O_5$

The agreement of this mechanism with our data is shown in Table IV where the experimental results are compared with the theoretical results derived from Reaction I.

TABLE IV

THEORETICAL AND EXPERIMENTAL QUANTUM YIELDS

	Theoretical from Reaction I	Theoretical (corrected for N_2O_3)	Experimental
$\Phi^{N_2}_{C_{15}H_{24}N_2O_4}$	0.50	0.46	0.38
$\Phi^{C_{15}H_{24}N_2O_2}_{C_{15}H_{24}N_2O_3}$	1.50	1.46	1.37
$N_2/C_{15}H_{24}N_2O_3$	0.33	0.32	0.29

However, the theoretical values must be corrected for the occasional escape of N_2O_3 as in Step IIa. One hundred molecules of liberated gas would consist of 14 molecules of N_2O_3 and 86 molecules of nitrogen. The N_2O_3 molecules would require 14 quanta and the nitrogen molecules would require 172 quanta, a total of 186 quanta. The corrected value for $\Phi^{N_2}_{C_{15}H_{24}N_2O_3}$ is $86/186$. The number of nitrosite molecules decomposed would be 272. The corrected value for $\Phi^{C_{15}H_{24}N_2O_3}_{C_{15}H_{24}N_2O_3}$ then is $272/186$. The ratio of N_2 to $C_{15}H_{24}N_2O_3$ decomposed would be $86/272$.

Discussion

Step I consists in the absorption of a quantum of light. Since most nitrosites and even liquid

(10) The symbols used below have the following meanings: β designates one of several isomers of caryophyllene [see Deussen. J. prakt. Chem., 114, 75 (1926)], * signifies a molecule in an activated state, and Δ refers to an isomer of the nitrosite as discussed later.

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.

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 mono-perchlorate, 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.

(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).