

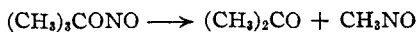
[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF UNION OIL COMPANY OF CALIFORNIA]

Photochemical Decomposition of *t*-Butyl Nitrite

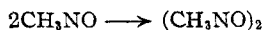
BY CLARENCE S. COE AND THOMAS F. DOUMANI

The photochemical decomposition of *t*-butyl nitrite has been studied in the vapor phase using a quartz mercury vapor lamp as a source of ultraviolet radiation. Some of the experimental technique and methods of analysis employed in these laboratories for the study of the determination of the primary products from the thermal cracking of hydrocarbons have been applied to this photochemical decomposition. This study involves distinguishing between the initial and the secondary reaction products by determining the composition of the products formed when only small percentages of the compound studied are decomposed at relatively low pressures. The mass spectrometer pattern for the gaseous decomposition products free of undecomposed *t*-butyl nitrite was obtained by subtracting the mass number contributions of the latter compound from the total pattern of the decomposition products. To determine which decomposition products were present, the mass spectrometer patterns for a large number of possible compounds were examined. Chemical tests were made on the residue in the quartz flask after each experiment and, where possible, solid derivatives were prepared for identification.

The initial photochemical decomposition products are acetone and nitrosomethane. During the decomposition this latter compound is constantly removed from the gas phase forming colorless long needles of m. p. 122° in dimeric form on the surface of the quartz reaction flask. Nitrosomethane and its dimer are believed to be new compounds. The initial reaction in the photochemical decomposition of *t*-butyl nitrite appears to be as follows



Dimerization of nitrosomethane appears to occur rapidly



The progress of this decomposition was followed by mass spectrometer analysis and manometrically by determining the total gas pressure in the

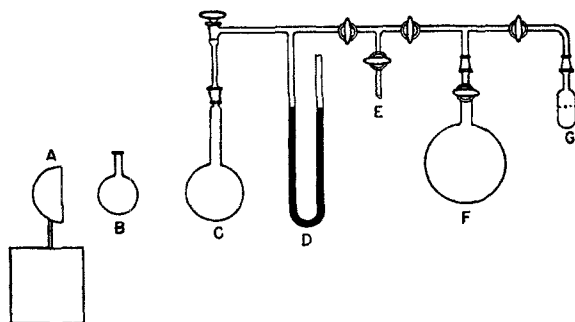


Fig. 1.—Diagram of apparatus.

irradiation quartz flask after various reaction times.

Experimental

Materials Used

***t*-Butyl Nitrite.**—Technical *t*-butanol was purified by fractional distillation followed by fractional crystallization. Five moles (370.6 grams) of *t*-butanol, m. p. 25.0–25.1°, was mixed with a solution of 5.5 moles (379.5 g.) of sodium nitrite dissolved in 1500 ml. of distilled water. Three moles (667 ml.) of 35% sulfuric acid was added during two hours to the bottom of the previous solution at 0° with stirring. The oil layer which was less dense than the aqueous layer was washed with water, aqueous sodium bicarbonate solution (5%), again with water, and finally dried with anhydrous sodium sulfate. The crude *t*-butyl nitrite (400 g.) was fractionated *in vacuo* in a packed column of about 10 theoretical plates. The composited fractions used in the irradiation studies had a b. p. of 34.0° (250 mm.), n_D^{20} 1.3687 and sp. gr. $^{20}_4$ 0.8671.

Acetone.—J. T. Baker analyzed, C. P. was used.

Nitromethane.—The product from Commercial Solvents Corporation was fractionated, b. p. 101–102°, n_D^{20} 1.3821.

Nitrogen Dioxide and Nitrous Oxide.—These gases were obtained in cylinders from the Matheson Company in 98% purity.

Nitric Oxide.—The method of Johnson and Giauque¹ was used.

Irradiation

The apparatus (Fig. 1) used for the irradiation experiments was assembled in a dark room which could be maintained at $25 \pm 1^\circ$. The radiation from a quartz mercury vapor lamp² (A) was passed through a quartz flask (B) containing distilled water and then into the quartz flask (C) of 350 ml. capacity filled with vapors of *t*-butyl nitrite. The quartz flask containing distilled water served to filter out infrared wave lengths and helped to focus the ultraviolet beam on the sample. The distance from "Uviarc" to focusing flask was 21.7 cm. and from the center of the latter to the center of the sample flask was 16.1 cm. The quartz flask (C) was connected to a mercury manometer (D) which was used to determine the total pressure therein. To introduce the *t*-butyl nitrite into the flask (C) the entire system was evacuated with a mercury diffusion pump through stopcock (E) in the presence of a few ml. of liquid *t*-butyl nitrite which was surrounded by liquid nitrogen in (G). The nitrite was then allowed to warm until the desired pressure was reached in the system. Gas samples were taken after varying irradiation times directly into evacuated 2-liter glass bulbs (F) which were covered with black tape to eliminate photochemical decomposition due to daylight. All samples were analyzed in a mass spectrometer within eight hours after collection.

In following the pressure change in the system during the photochemical decomposition the mercury manometer was replaced by a more sensitive combination mercury-oil manometer.

To prepare sufficient amounts of dimeric nitrosomethane for a determination of some of its properties the following procedure was found effective. About one milliliter of liquid *t*-butyl nitrite was condensed into the bottom of the

(1) H. L. Johnson and W. F. Giauque, *THIS JOURNAL*, **51**, 3195 (1929).

(2) "Uviarc," 360 watt, 6 inch (General Electric Company). The principal lines are reported to lie between 2345 and 5790 Å.

TABLE I^a
 PHOTOCHEMICAL DECOMPOSITION OF *t*-BUTYL NITRITE

Experiment	Reaction time, min.	Pressure, mm.		Analysis of gaseous reaction product, mole %			
		Initial	Final	<i>t</i> -C ₄ H ₉ ONO	(CH ₃) ₂ CO	<i>t</i> -C ₄ H ₉ OH	CH ₃ NO ₂ , NO ₂ , NO, CH ₃ NO, etc.
P-9692	30	154.9	160.1	91.1	4.5	1.6	2.8
P-9693-2	5	159.7	160.3	96.4	1.0	0.2	2.4
P-9696-1	5	48.0	48.2	97.0	2.0	0.4	0.6
Q-2310-2	7.5	46.4	47.2	95.1	3.3	0.6	1.0
Q-2306-5	10	46.4	46.6	93.9	4.4	0.7	1.0
Q-2312-6	20	46.5	48.6	88.0	9.0	0.0	3.0
Q-2328-3	40	46.4	48.4	77.0	17.0	1.0	5.0
Q-2328-5	60	46.6	48.8	74.0	25.0	1.0	0.0
Q-2329-2	120	46.9	50.1	50.0	50.0	3.0	4.0
Q-2333-2	290	34.4	39.7	5.5	71.7	7.3	15.5
Q-2333-3	386	35.0	48.0	1.8	57.9	7.4	32.9

^a Detailed data for the spectrometer analyses may be obtained from the authors on request.

evacuated quartz flask. The reaction vessel was then irradiated with the "Uviarc," shielding the liquid from direct radiation. The liquid *t*-butyl nitrite served as a reservoir for the production of the gaseous nitrite. The crystals were deposited in much larger quantities in the quartz flask than when the homogeneous nitrite vapors were irradiated.

Results

Data on the photochemical decomposition of *t*-butyl nitrite vapor at various pressures and irradiation times are given in Table I. A plot showing the decrease in the *t*-butyl nitrite and the increase in the acetone percentages with time is given in Fig. 2.

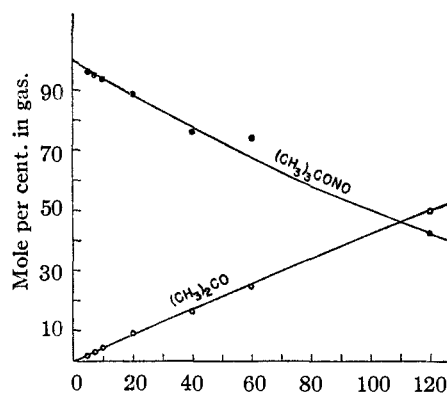


Fig. 2.—Effect of irradiation time.

A pressure-time curve for the photochemical decomposition of *t*-butyl nitrite is shown in Fig. 3. This first irradiation period of about 200 minutes is characterized by the production of predominantly initial decomposition products. Secondary decomposition products are principally formed during the second reaction period from 200 to about 320 minutes. The practically constant pressure state is finally reached after about 400 minutes when compounds substantially stable to the ultraviolet light are present. For this experiment small crystals of nitrosomethane dimer were noticeable with the naked eye after about 120 min-

utes of irradiation. These crystals grew to well-defined needles until after about 290 minutes they commenced to be transformed to an amorphous deposit of trimeric formaldoxime. Continued irradiation caused a practically complete conversion of the dimeric nitrosomethane to the latter compound after about 420 minutes. A photograph of some crystals of nitrosomethane dimer in the quartz irradiation flask is shown in Fig. 4.

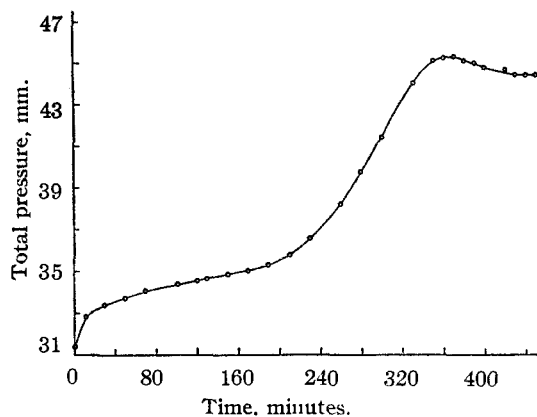


Fig. 3.—Total pressure-time plot.

The irradiated vapors of *t*-butyl nitrite in the quartz flask was shaken with an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride forming the hydrazone of m. p. 125.6° (cor.). Mixed m. p. with pure acetone 2,4-dinitrophenylhydrazone was the same.

Anal. Calcd. for C₉H₁₀N₄O₄; C, 45.38; H, 4.23. Found: C, 45.41; H, 4.50.

Some Properties of Dimeric Nitrosomethane.—Several grams of crystals was collected from a series of the irradiation experiments and crystallized from ethanol as colorless needles, m. p. 122.0–122.2° (cor.). This compound is very soluble in ethanol, moderately soluble in water or acetone, slightly soluble in ethyl ether, benzene or carbon tetrachloride, and insoluble in pentane.

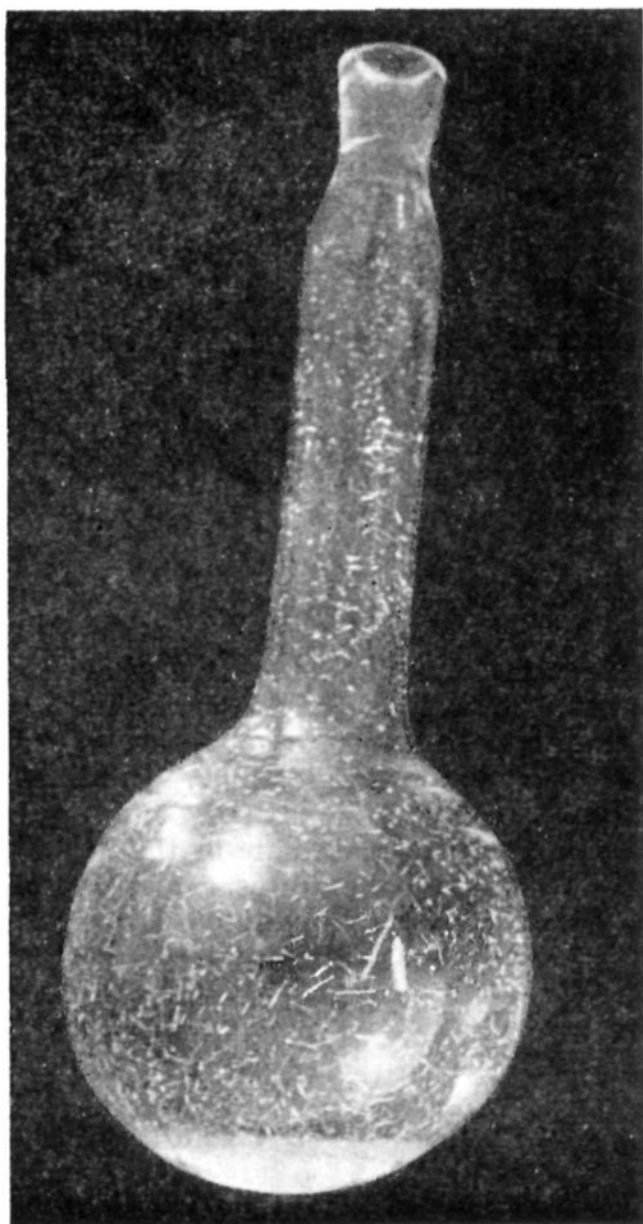
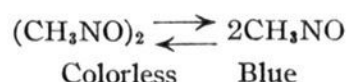


Fig. 4.—Crystals of dimeric nitrosomethane in quartz reaction flask.

*Anal.*³ Calcd. for $(\text{CH}_3\text{NO})_2$: C, 26.66; H, 6.71; N, 31.10; mol. weight, 90.1. Found: C, 26.94; H, 7.01; N, 31.15; mol. weight, 93.4 (benzophenone as solvent).

The mass spectrometer numbers for this dimer were obtained by admitting vapors from the finely crushed powder at room temperature into the head of the mass spectrometer at low pressure. The mass numbers 90, 75, 60, 45, 30, and 15 were obtained.

When nitrosomethane dimer is heated above its melting point a blue color is noticeable, especially in the vapor. Likewise, when this dimer is heated in organic solvents, such as toluene, a blue color is produced. The colorless solution is restored by cooling. This reversible color change may be represented by the equation



(3) Low N values are obtained by the usual micro-Dumas or micro-Kjeldahl methods. Friederich's micro-Kjeldahl method with hydriodic acid was used (Pregl-Grant, "Quantitative Organic Microanalysis," The Blakiston Co., Philadelphia, Pa., 1946, p. 82).

Prolonged heating of dimeric nitrosomethane above its melting point converts it to trimeric formaldoxime, insoluble in ethanol



Nitrosomethane dimer forms a blue color when tested with diphenylamine in concentrated sulfuric acid.

Discussion

Both the experimental data and the proposed mechanism for the photochemical decomposition of *t*-butyl nitrite of Thompson and Dainton⁴ are at variance with the results of the present investigation. Their mechanism involving the formation of hyponitrous acid does not explain the formation of nitrosomethane or acetone. None of the products propylene, formaldehyde, ethane or ethylene required by their mechanism could be found in the gaseous decomposition products.

The complete absence of ethane in the decomposition products seems to indicate that the nitrosomethane is probably formed intramolecularly. If the nitrosomethane were formed by the combination of free methyl radicals with nitric oxide the formation of at least some ethane might be expected.

The mass spectrometer pattern for nitrosomethane dimer serves as further evidence for its constitution. Loss of a methyl radical of mass 15 from dimeric nitrosomethane of mass 90 leaves a mass of 75. Removal of a second methyl radical leaves 60, whereas depolymerization of the dimer produces two molecules of monomeric nitrosomethane of molecular weight 45. Removal of a methyl radical from the monomer produces the 30 mass.

Previous workers⁵ have postulated the existence of nitrosomethane in explaining the inhibition of some chain reactions by nitric oxide. Isolation of this compound serves to substantiate some of these mechanisms.

The development of alternative methods for the synthesis of nitrosomethane dimer is being considered as well as its isomerization to trimeric formaldoxime. The photochemical decomposition of some other organic nitrites is being checked to determine whether nitroso compounds are involved.

Acknowledgment.—We wish to thank the management of the Union Oil Company of California for permission to publish this paper. We are especially grateful to our analytical department for their generous assistance.

Summary

1. The photochemical decomposition of *t*-butyl nitrite has been studied in the vapor phase at 25° and at pressures of about 50 mm. using a quartz mercury vapor lamp.

(4) H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1551 (1937).

(5) H. A. Taylor and H. Bender, *J. Chem. Phys.*, **9**, 761 (1941).

2. Acetone and nitrosomethane were found to be initial products of the decomposition. The latter new compound was identified as the hitherto unknown crystalline dimer.

3 Some of the properties of nitrosomethane and its dimer have been determined.

WILMINGTON, CALIFORNIA

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Copolymerization. IV. Effects of Temperature and Solvents on Monomer Reactivity Ratios

BY FREDERICK M. LEWIS, CHEVES WALLING, WILLIAM CUMMINGS,¹ EMORENE R. BRIGGS² AND FRANK R. MAYO

Previous papers from this Laboratory and elsewhere³ have shown that the behavior of monomers in free radical type copolymerizations may be described accurately by the copolymerization equation^{3a,4,5}

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]r_1[M_1] + [M_2]}{[M_2]r_2[M_2] + [M_1]} \quad (1)$$

where $[M_1]$ and $[M_2]$ are concentrations of unreacted monomers, r_1 is the ratio of the rate constants for the reaction of an M_1 -type radical with M_1 and M_2 , respectively, and r_2 is the ratio for reaction of an M_2 -type radical with M_2 and M_1 , respectively. The quantities r_1 and r_2 have been designated *monomer reactivity ratios*, and it should be noted^{3b} that a comparison of the *reciprocals* of a series of monomer reactivity ratios for a particular radical with a number of monomers yields the *relative reactivities* of the monomers toward that radical. If such series for all radicals were the same, *i. e.*, if, in general, $r_1r_2 = 1$, Equation (1) would reduce to the simpler form earlier proposed by Wall.⁶ However, a striking feature of free radical copolymerizations is that, in many pairs, each monomer prefers to react with the opposite type radical. This "alternating effect," which can be discussed qualitatively in terms of r_1r_2 products (r_1r_2 being zero for complete alternation), appears to be an additional effect superimposed upon a fundamental order of monomer reactivity,^{3b} and Price⁷ has suggested, on the basis of the data available at the time, that it arises from polar interaction between radical and monomer. The present series of nine papers increases five-fold the number of monomer pairs for which monomer

reactivity ratios are available. The results give partial support to Price's suggestion and permit a much more detailed discussion of copolymerization phenomena than has hitherto been possible.

The present paper discusses refinements in techniques and in the treatment of data which have been developed in this Laboratory during the past three years and presents measurements of the temperature coefficients of monomer reactivity ratios for five monomer pairs. It also reports more precise measurements of the effects of solvents on the monomer reactivity ratios for styrene and methyl methacrylate.

The next three papers, V-VII, describe new experiments on twenty-nine monomer pairs. In VIII, all of these data are reviewed and the theoretical implications discussed in terms of monomer activity and polarity series. Copolymerization IX presents and discusses experiments on the relative reactivities in copolymerization of *cis* and *trans* isomers. The last three papers, X-XII, are a study of the effect of nuclear substitution on the reactivity of styrene in copolymerization. Here, measurements on thirty-six systems throw further light on the nature of the "alternating effect" in copolymerization.

Experimental

Materials.—Diethyl maleate and diethyl fumarate were Eastman Kodak Co. materials, melting points -12 to -11 and 0 to 1° , respectively. They were used without further purification. Styrene, methyl methacrylate and methyl acrylate were commercial materials, fractionally distilled and stored in the ice-box until used. *p*-Chlorostyrene was prepared by the decarboxylation of *p*-chlorocinnamic acid. Its preparation and physical properties are described elsewhere.⁸

Polymerization Technique.—Polymerizations were carried out in duplicate or triplicate on 1:4 and 4:1 molar ratios of monomers in sealed tubes in absence of air, essentially as described in previous papers in this series.^{3a} At 60° , 0.1 mole % benzoyl peroxide was used as catalyst, at 131° , no catalyst except for the styrene-methyl methacrylate system where 0.1% acetone peroxide was added. All polymers were soluble in benzene and were isolated by the frozen benzene technique.⁹ Results of all experiments reported here are listed in Tables I and II.

Experimental Errors.—Extensive experience in this laboratory has shown that, although any set of experiments may give a very small intersection in the graphical

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(2) Present address, R. F. D. 2, Guilford, Conn.

(3) (a) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944); (b) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945); (c) Bartlett and Nozaki, *ibid.*, **68**, 1495 (1946); (d) Alfrey, Goldberg and Hohenstein, *ibid.*, 2464; (e) Fordyce and Chapin, *ibid.*, **69**, 581 (1947). Further references will be found in these papers.

(4) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Wall, *THIS JOURNAL*, **66**, 2050 (1944).

(5) Hereafter in this series the new nomenclature for copolymerization constants, *cf.* Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946), is used. Thus, M_1 , M_2 , r_1 and r_2 correspond to S , M and μ in previous papers.

(6) Wall, *ibid.*, **63**, 1862 (1941).

(7) Price, *J. Polymer Sci.*, **1**, 83 (1946).

(8) Walling and Wolfstirn, *THIS JOURNAL*, **69**, 852 (1947).

(9) Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).