TABLE IV

PHOTOLYSIS OF ISOBUTANE-d_{10} IN THE PRESENCE OF ETHYLENE

i-C_4D_{10}, mm.	C_2H_4, mm.	Exciting lines	Exposure time t, min.	Relative amounts of hydrogen produced H_2	HD	D_2	Percentage absorption (α) by i-C_4D_{10}	$D_2/t\alpha$[a] (arbitrary units)
10.3	0	Xe	30	10	18	305	100	1.00
10.0	10.0	Xe	60	646	36	170	49.5	0.56
10.1	0	Xe	30	2	18	295	100	0.97

[a] The quantity $D_2/t\alpha$ represents the relative quantum yield of deuterium production.

is equal to 1.7 ± 0.1, which agrees reasonably well with the value 1.9 measured by Wijnen.[10]

Other Processes.—Two main processes can be considered for the formation of propylene

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} CH_4 + C_3H_6 \qquad (4)$$

$$2i\text{-}C_3H_7 \longrightarrow C_3H_8 + C_3H_6 \qquad (5)$$

Equal amounts of methane and propylene, and of propane and propylene, should be produced from the reactions 4 and 5, respectively. Therefore, the yield of ($CH_4 + C_3H_8$) must be equal to the yield of C_3H_6. From Table I, the yield ($CH_4 + C_3H_8$) = 0.61 is found in reasonable agreement with the yield of C_3H_6 = 0.71.

Isobutene is formed by the reactions

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} i\text{-}C_4H_8 + H_2 \qquad (6)$$

$$2C_4H_9 \longrightarrow i\text{-}C_4H_8 + i\text{-}C_4H_{10} \qquad (7)$$

Neopentane and isopentane probably are produced from the reactions 8 and 9

$$CH_3 + t\text{-}C_4H_9 \longrightarrow \text{neo-}C_5H_{12} \qquad (8)$$

$$CH_3 + i\text{-}C_4H_9 \longrightarrow i\text{-}C_5H_{12} \qquad (9)$$

Ethylene probably is formed by the expulsion of two methyl radicals from isobutane

$$i\text{-}C_4H_{10} \xrightarrow{h\nu} 2CH_3 + C_2H_4 \qquad (10)$$

No reliable isotopic analysis of ethylene could be made since the amount was small, but it is certain that [C_2H_3D] is small in comparison with [C_2D_4] in the photolysis of the 50:50 mixture of i-C_4H_{10}–i-C_4D_{10}. The result supports reaction 10.

The formulas obtained from the products analysis (Table I) are $C_4H_{10.9}$ and $C_4H_{11.2}$ at the Xe and Kr lines, respectively. They are in good agreement with that for isobutane, indicating that amounts of unobservable alkenes and higher alkanes are small.

Other products, isobutene, *cis*-butene-2 and *n*-butane, amount to less than 5% of the total hydrogen. It is difficult to explain their formation unless extensive rearrangement of excited species occurs. These products may be coming from secondary reactions.

Acknowledgments.—The authors wish to thank Dr. J. R. McNesby for his valuable comments on this work.

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[10] M. H. J. Wijnen, *J. Chem. Phys.*, **28**, 271 (1958).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, CELANESE CHEMICAL CO., A DIVISION OF CELANESE CORPORATION OF AMERICA, CLARKWOOD, TEX.]

Photolysis of Alkyl Nitrites. I. *tert*-Butyl Nitrite

BY G. R. MCMILLAN[1]

RECEIVED MAY 31, 1962

Quantum yields have been measured in the vapor phase photolysis of mixtures of *tert*-butyl nitrite and nitric oxide. An excited radical mechanism is proposed. At 99° with incident light of 2537 Å., the quantum yield of excited *tert*-butoxy radical formation is unity. The excited radicals decompose to acetone and methyl with an activation energy of a few kcal. Collisional deactivation can be observed at quite low pressures. The range of deactivation efficiencies of various gases is suggestive of the relative efficiencies reported for deactivation of molecules in very high states of vibrational excitation. No evidence for abstraction of hydrogen by the excited radicals could be obtained. The importance of excited radical decomposition increases with temperature due to two influences: an increase in rate of radical decomposition at higher temperatures and an increase in the fraction of excited radicals produced in the primary process.

Introduction

Alkyl nitrites have been the subject of many photochemical studies, but few quantitative investigations and no detailed quantum yield measurements have been reported. Recent interest in these compounds, has been mostly in the fields of air pollution[2] and organic preparations.[3]

tert-Butyl nitrite seemed the simplest nitrite to study because: (1) something is known of the reactions of the *tert*-butoxy radical, an expected product of the primary process; (2) a disproportionation step between the *tert*-butoxy radical and nitric oxide does not occur[4,5]; and (3) unlike the primary and secondary nitrites, *tert*-butyl nitrite at room temperature is almost a single species, that is, almost entirely the *trans* isomer.[6]

tert-Butyl nitrite exhibits two regions of absorption[7] in the near ultraviolet: a banded region extending from 4100 to 3200 Å. and a supposedly

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[1] Evans Chemical Laboratory, The Ohio State University, Columbus 10, Ohio.

[2] P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, Inc., New York, N. Y., 1961.

[3] A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 35 (1962).

[4] J. B. Levy, *Ind. Eng. Chem.*, **48**, 762 (1956).

[5] G. R. McMillan, *J. Am. Chem. Soc.*, **84**, 2514 (1962).

[6] P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

[7] H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937).

continuous absorption becoming very strong below 3000 Å.

The nature of the primary process has not been completely clarified. There appears to be a wave length effect[7,8]; and in most studies, the light employed has not been even approximately monochromatic. Coe and Doumani,[9] and other workers,[10] explained the results of the photolysis of *tert*-butyl nitrite on the basis of the primary process

$$(CH_3)_3CONO + h\nu \longrightarrow CH_3COCH_3 + CH_3NO$$

More recently, the photodecomposition of alkyl nitrites has been interpreted[11] in terms of bond scission to form an alkoxy radical and nitric oxide, a step analogous to that known to occur in the thermolysis of these compounds. Tarte[8] believed that either primary process could occur, depending on the wave length of the incident light and the structure of the alkyl nitrite. Recent work on photolysis of nitrites in solution confirms the formation of alkoxy radicals under some conditions.[3]

Evidence for the importance of excited alkoxy radicals was found in photolysis studies of esters[12] and peroxides.[5,13] *tert*-Butyl nitrite, formed as an early product during irradiation of di-*t*-butyl peroxide–nitric oxide mixtures,[5] undergoes secondary decomposition under conditions that suggest either the intervention of a hot radical effect or a molecular split such as that proposed by Coe and Doumani.

Experimental

Samples of *tert*-butyl nitrite prepared by the reaction of *tert*-butyl alcohol with either nitrous acid[14] or nitrosyl chloride[15] gave the same quantum yields upon vapor phase photolysis. The samples were distilled at reduced pressure and stored over mercury in a cold, dark place.

Nitric oxide from Matheson Chemical Co. was passed over silica gel[16] cooled to −79° and finally fractionally distilled in the vacuum line. Nitric oxide containing 96% ^{15}NO was obtained from the Isomet Corporation, Palisades Park, N. J.

Ethane was Phillips Research Grade.

Tank nitrogen was passed over calcium sulfate, over hot, freshly conditioned copper gauze, and finally through traps cooled in liquid nitrogen.

All photolyses were carried out in a quartz vessel of diameter 5 cm., volume 236 ml., using the Hanovia type A mercury lamp.

Light leaving the vessel was monitored by an RCA 935 phototube and a pen recorder. A permanent record was made of a pen deflection proportional to the light intensity passing from the vessel during the illumination. It was also necessary to record I_i and I_f, the deflections corresponding to the intensity before and after the illumination (the vessel being empty).

The filter combination used to isolate λ 2537 Å. radiation consisted[17] of a 1-cm. optical path of potassium triiodide solution, a 12-cm. optical path of chlorine gas (275 mm. pressure) and a 3-mm. thickness of Corning Glass 9863 (C.S. 7-54). Two special problems arise in using this filter for quantum yield determination in alkyl nitrite photolyses: (1) The transmission of the KI_3 solution decreases nonlinearly during an irradiation period. This is readily corrected for by measuring the decay of the filter with the reaction cell empty, then fitting this decay curve to the I_i and I_f readings and the recorder trace obtained during the illumination period of each experiment. The area corresponding to the number of quanta absorbed is thusly bounded. (2) The filter transmits a small amount of the λ 4047 Å. mercury line, to which the phototube responds and which is weakly absorbed by the nitrite. A special experiment showed that this small amount of high wave length light caused negligible acetone formation; hence the contribution of this radiation could be subtracted from the area under the recorder trace. In all photolyses, except the special low pressure experiment to be described, the λ 2537 Å. radiation was completely absorbed.

The incident light intensity was measured using the acetone actinometer, taking $\Phi_{CO} = 1$ at 120°. The acetone pressure used was a few mm. below the vapor pressure at room temperature.

A few experiments were carried out at 3130 Å. using a filter composed of a solution of 105 g./l. of $NiSO_4 \cdot 6H_2O$ and 30 g./l. of $CoSO_4 \cdot 7H_2O$, both in a 5-cm. optical path, together with a 3-mm. thickness of Corning Glass 9863 and 5 mm. of Pyrex.

The reactants were degassed and mixed by repeated expansion into a large bulb. The quantum yields were the same with or without subsequent interruption of the irradiation for mixing.

After illumination, nitrogen was separated at −210° and nitric oxide at −180°. Condensable products were analyzed by gas chromatography. Considerable hydrolysis of the nitrite occurred on all G.C. columns tested.

Results

Mixtures of *tert*-butyl nitrite vapor with nitric oxide were exposed to light of λ 2537 Å. The main product is acetone; methyl nitrate and nitrogen are found in lesser quantities. Nitromethane appears to be a trace product.

In the usual experiment, no conclusions may be drawn about *tert*-butyl alcohol production because the substance is always found due to hydrolysis in the G.C. apparatus. A special experiment was carried out to check alcohol formation. A mixture of *tert*-butyl nitrite (pressure 3 mm.), nitric oxide (15 mm.), and ethane (100 mm. to act as a hydrogen donor) was irradiated for about 12 hr. at 26°. Even this small amount of nitrite underwent some hydrolysis on the G.C. column, so the observed quantum yield of *tert*-butyl alcohol, 0.003, must be considered a maximum.

The methyl nitrate quantum yield was 0.07 in the prolonged photolysis.

Nitrogen, like methyl nitrate, is a minor product. In a series of five experiments at 26°, with concentrations of *tert*-butyl nitrite and nitric oxide of 4.9×10^{17} molecules/ml. and conversions about 2%, Φ_{N_2} was 0.13 ± 0.01 (std. dev.).

No evidence for nitrosomethane dimer was obtained. The transmission of the reaction cell windows was not decreased at the end of a photolysis, even with the cell at room temperature.

Only acetone was measured quantitatively in most experiments (Table I). Figures 1 through 3 show the dependence of the acetone quantum yield upon concentrations of nitric oxide, *tert*-butyl nitrite and added nitrogen and ethane. The absorbed intensity in all experiments was approximately 4×10^{12} quanta/ml./sec. The conversion at the lowest nitrite concentration was 1%. Constant

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(8) P. Tarte, *Bull. soc. roy. sci. Liège*, **22**, 226 (1953).

(9) C. S. Coe and T. F. Doumani, *J. Am. Chem. Soc.*, **70**, 1516 (1948).

(10) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

(11) J. A. Gray and D. W. G. Style, *Trans. Faraday Soc.*, **48**, 1137 (1952); P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, **63**, 2071 (1959).

(12) M. H. J. Wijnen, *J. Am. Chem. Soc.*, **82**, 1847 (1960).

(13) G. R. McMillan, *ibid.*, **83**, 3018 (1961).

(14) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 305.

(15) R. H. Pickard and H. Hunter, *J. Chem. Soc.*, 434 (1923).

(16) E. E. Hughes, *J. Chem. Phys.*, **33**, 1531 (1961).

(17) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 69.

extent of decomposition was maintained in most experiments, but, in the runs in which nitrite concentration was varied, the range of extent of decomposition was about a factor of three.

Figure 4 shows the temperature dependence of the acetone quantum yield under standard conditions of concentration, light intensity and % conversion.

When the nitrite is illuminated with light of λ 3130 Å. the acetone quantum yield falls to about 0.2. The nitrite and nitric oxide concentration was 4.9 × 10^{17} molecules/ml. in these runs.

No luminescence was found by visual examination at either wave length.

TABLE I

PHOTOLYSIS OF *tert*-BUTYL NITRITE-NITRIC OXIDE MIXTURES

λ = 2537 Å., I_a = 4 × 10^{12} quanta/ml./sec.

10^{-17} [nitrite], molecules/ml.	10^{-17}[NO], molecules/ml.	10^{-17}[additive], molecules/ml.	$\Phi_{CH_3COCH_3}$
		T = 26°	
5.5	4.9	.....	0.81
8.9	4.9	.....	.83
13.9	4.9	.....	.84
18.7	4.9	.....	.73
26.5	4.9	.....	.80
35.9	4.9	.....	.66
40.1	4.9	.....	.74
44.3	4.9	.....	.73
56.8	4.9	.....	.64
4.9	0.0	.....	.85
4.9	1.3	.....	.85
4.9	2.6	.....	.85
4.9	4.9	.....	0.84, 0.81, 0.79
4.9	6.5	.....	0.82
4.9	14.5	.....	.82
4.9	19.4	.....	.79
4.9	33.3	.....	.71
4.9	4.9	36.5 N_2	.85
4.9	4.9	38.8 N_2	.83
4.9	4.9	76.6 N_2	.81
4.9	4.9	94.3 N_2	.74
4.9	4.9	110.0 N_2	.73
4.9	4.9	32.6 C_2H_6	.79
4.9	4.9	61.4 C_2H_6	.75
4.9	4.9	72.7 C_2H_6	.74
4.9	4.9	89.5 C_2H_6	.71
4.9	4.9	119.2 C_2H_6	.63
		T = 79°	
4.9	4.9		0.99, 0.96, 0.89, 0.87
17.3	4.9		0.94
21.1	4.9		.95
32.1	4.9		.95
32.3	4.9		.87
37.5	4.9		.92
44.9	4.9		.85
46.0	4.9		.89
46.3	4.9		.85

Discussion

(a) Reactions Probably Important

$$(CH_3)_3CONO + h\nu \longrightarrow \alpha_0(CH_3)_3CO^* + [1 - \alpha_0](CH_3)_3CO + NO \quad (1)$$

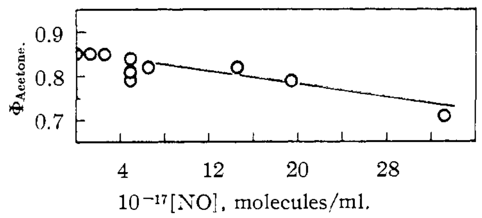

Fig. 1.—Photolysis of *tert*-butyl nitrite–nitric oxide mixtures at 26° and λ 2537 Å. Dependence of acetone quantum yield on nitric oxide concentration. *tert*-Butyl nitrite concentration is 4.9 × 10^{17} molecules/ml.

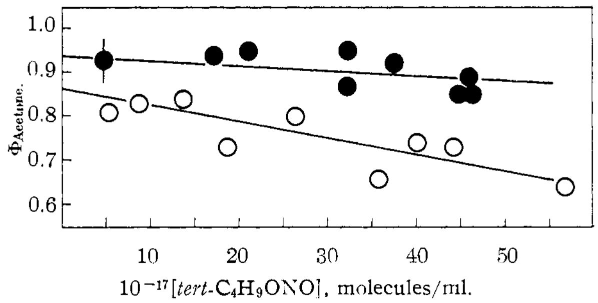

Fig. 2.—Dependence of acetone quantum yield on *tert*-butyl nitrite concentration at 26 (○) and 79° (●); concentration of nitric oxide, 4.9 × 10^{17} molecules/ml.

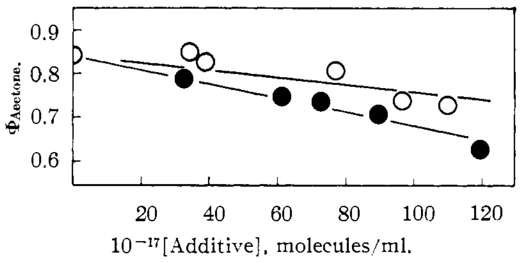

Fig. 3.—Effect of added nitrogen (○) and ethane (●) on acetone quantum yield at 26° and λ 2537 Å. Concentrations of *tert*-butyl nitrite and nitric oxide were 4.9 × 10^{17} molecules/ml.

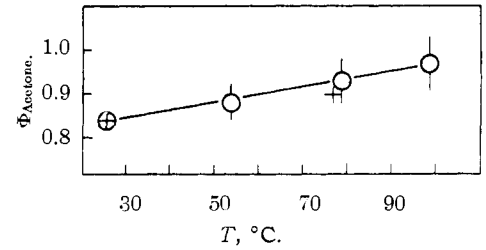

Fig. 4.—Temperature effect on the acetone quantum yield (○). Concentrations of *tert*-butyl nitrite and nitric oxide were 5 × 10^{17} molecules/ml. The crosses represent the hot radical fraction of *tert*-butoxy radicals formed in photodecomposition of di-*tert*-butyl peroxide at the same wave length (2537 Å.), but concentrations of peroxide of 6 × 10^{17} and of nitric oxide 4–5 × 10^{17} molecules/ml. The values of the hot radical fraction from the peroxide study have been scaled +0.28 unit to fit the two curves at 26°.

$$(CH_3)_3CO^* \longrightarrow CH_3COCH_3 + CH_3 \quad (2)$$

$$(CH_3)_3CO^* + (CH_3)_3CONO \longrightarrow (CH_3)_3CO + (CH_3)_3CONO \quad (3)$$

$$(CH_3)_3CO^* + NO \longrightarrow (CH_3)_3CO + NO \;? \quad (4)$$

$$(CH_3)_3CO^* + M \longrightarrow (CH_3)_3CO + M \qquad (5)$$

$$(CH_3)_3CO + NO \longrightarrow (CH_3)_3CONO \qquad (6)$$

$$CH_3 + NO \longrightarrow CH_3NO \longrightarrow \text{products} \qquad (7)$$

It is supposed that a part of the *tert*-butoxy radicals formed in the primary process are in some unspecified excited state from which they may decompose rapidly to acetone and methyl. The excited radical fraction, α_0, will in general be dependent upon temperature as well as upon the wave length of the incident light. The simple energy distribution wherein the radicals are either excited or unexcited has for many years proved useful in treating hot radical effects.[18]

The primary process is written without an intermediate excited molecule of appreciable lifetime, a safe postulate if one could be sure the absorption is truly continuous. Actually, the mechanism to be developed depends upon the safer assumption that decomposition to radicals occurs in a time short compared with the time between collisions. If the absorption is continuous, the primary quantum yield, φ, must of course be unity. In the present experiments, the low pressure acetone quantum yield provides a lower limit for φ. At 2537 Å., φ must be $\geqq 0.84$ at 26° and $\geqq 0.97 \pm 0.04$ at 99°.

Deactivation steps 2, 4 and 5 account for the decrease in Φ_{acetone} with an increase in concentration of *tert*-butyl nitrite, nitric oxide or the added gases nitrogen and ethane.

Unexcited *tert*-butoxy radicals, formed in the primary process together, with those formed by collisional deactivation, re-form *tert*-butyl nitrite by step 6. An attempt was made to measure the quantum yield of 6 by measuring the photo-exchange between $(CH_3)_3CONO$ and ^{15}NO. The correction for dark exchange is negligible; but large, irreproducible amounts of exchange were observed upon irradiation of the mixture. One of the complications is probably the dark exchange between *tert*-butyl nitrite and the products of reaction 7.

(b) Reactions Probably Unimportant

$$\text{(i)}\quad (CH_3)_3CONO + h\nu \longrightarrow CH_3COCH_3 + CH_3NO \qquad (8)$$

The primary process favored in early work cannot be completely ruled out, but if the spectrum is continuous or if the lifetime of any excited molecule is short, this process would not seem to be important, since it allows no deactivation step, hence no ready explanation of the effect of pressure on the acetone quantum yield.[19]

$$\text{(ii)}\quad (CH_3)_3CO \longrightarrow CH_3COCH_3 + CH_3 \qquad (9)$$

Unexcited *tert*-butoxy radicals are scavenged so rapidly by nitric oxide that 9 probably does not occur under conditions of the present experiments. Nitric oxide at a pressure of a few mm. removes all the *tert*-butoxy radicals formed by thermal decomposition of di-*tert*-butyl peroxide,[20] at least at temperatures below 150°.

$$\text{(iii)}\quad (CH_3)_3CO^* + RH \longrightarrow (CH_3)_3COH + R \qquad (10)$$

The analytical method used did not usually permit analysis for *tert*-butyl alcohol. In the prolonged experiment previously described, the maximum alcohol quantum yield was 0.003, indicating that 10 does not occur appreciably, at least at low nitrite pressure. Excited *tert*-butoxy radicals formed by photolysis of di-*tert*-butyl peroxide show no tendency to abstract hydrogen, even from propylene.[5] Barton, *et al.*,[21] proposed a rapid intramolecular hydrogen abstraction by excited alkoxy radicals formed by photolysis of nitrites in solution.

(c) **Evaluation of α_0.**—The quantity α_0 is evaluated as the acetone quantum yield in the absence of deactivating collisions; hence it corresponds to the intercepts of Fig. 2 corrected for the deactivating effect of nitric oxide. At 79°, deactivation is slight and may be neglected; α_0 is thus 0.94. At 26°, Fig. 1 shows that a concentration of 4.9×10^{17} molecules/ml. of nitric oxide reduces Φ_{acetone} by 0.01; α_0 at 26° is therefore $0.86 + 0.01 = 0.87$.

Figure 4 shows the acetone quantum yield as a function of temperature. At the low reactant concentrations used, the increase with temperature is mainly attributable to an increase in α_0. The "hot radical fraction" of *tert*-butoxy radicals in the di-*tert*-butyl peroxide photolysis[5] at 2537 Å. is plotted to show the similarity of dependence. The peroxide results have been suitably scaled.

It is curious that a small energy increase in the nitrite molecules could have such a large effect on the energy distribution of the radicals formed by photolysis.

(d) **Deactivation Processes.**—The data in Figs. 1–3 may be recast in the form $1/\Phi_{\text{acetone}} = a + b[c]$, in conformity with an equation derived from the mechanism

$$1/\Phi_{CH_3COCH_3} = 1/\alpha_0 + k_3[\text{nitrite}]/\alpha_0 k_2 + k_4[NO]/\alpha_0 k_2 + k_5[M]/\alpha_0 k_2$$

Since α_0 has been determined, the ratios k_i/k_2 may be computed. These are given in Table II.

The constants k_i may be approximated as the product of the specific collision number and a deactivation efficiency peculiar to the deactivating molecule. The rate constant ratios may then be corrected for the different number of collisions/unit time the different deactivating gases undergo with an excited radical.[22] The ratios are then placed on a relative basis to give the relative, collision for collision deactivation efficiencies shown in Table II.

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[18] D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).

[19] A further attempt to test the participation of step 8 was made by examining the products derived ultimately from nitrosomethane. This compound may add two molecules of nitric oxide and eventually yield nitrogen, methyl nitrate and possibly other products (L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, **56**, 682 (1960)). The most reasonable course for the over-all reaction predicts that, exchange being absent, the molecular nitrogen should contain one nitrogen atom originally present in the nitrosomethane. Therefore, if the photolysis is carried out in the presence of nitric oxide enriched in ^{15}N, the composition of the nitrosomethane, hence of the nitrogen, will be different for the primary processes 1 and 8. The observed isotopic distribution was in fair agreement with that expected if only 1 takes place. Unfortunately, the agreement proves nothing definite, for the same distribution would result if 8 were followed by equilibration of nitrosomethane (or other intermediate) with the nitric oxide present.

[20] F. W. Birss, C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A239**, 154 (1957); also unpublished results of the author.

[21] D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **83**, 4076 (1961).

[22] The collision diameters in Å. chosen for this calculation were: $(CH_3)_3CONO$, 6.5; $(CH_3)_3CO^*$, 5.5; N_2, 3.68; C_2H_6, 4.30; NO, 3.7.

TABLE II

DEACTIVATION OF EXCITED *tert*-BUTOXY RADICALS BY SEVERAL GASES

$T = 26°, \lambda = 2537$ Å.

Deactivating gas	$10^{20}\ k_1/k_2$, ml./molecule	Rel. deact. efficiency on coll./coll. basis
$(CH_3)_3CONO$[a]	5.6	1.0
NO	5.0	1.1
C_2H_6	2.4	0.46
N_2	1.1	0.23

[a] At 79°, $k_1/k_2 = 1.2 \times 10^{-20}$ ml./molecule.

The range of efficiencies from a diatomic molecule to a polyatomic molecule is quite small. Such a narrow range is reminiscent of that found for deactivation of molecules excited to very high vibrational levels.[23]

Nitric oxide has an unexpectedly high efficiency for a diatomic molecule. This indicates that 4 is probably not a simple deactivation step. It does not seem possible to choose among several suggestions as to the exact nature of this reaction.

If every collision between the excited radical and a *tert*-butyl nitrite molecule leads to deactivation, an upper limit of k_2 of 8×10^9 sec.$^{-1}$ may be computed. For comparison, the rate constant for decomposition of the thermalized *tert*-butoxy radical at 26° is probably not greater than 10^3 sec.$^{-1}$.

From the values of k_3/k_2 at 26° and 79°, $E_2 - E_3$ is found to be 6.1 kcal./mole.

$$(CH_3)_3CO^* \longrightarrow CH_3COCH_3 + CH_3 \qquad (2)$$

$$(CH_3)_3CO^* + (CH_3)_3CONO \longrightarrow (CH_3)_3CO + (CH_3)_3CONO \qquad (3)$$

The apparent activation energy of deactivation steps like 3 is often taken to be zero. This will not generally be the case, since k_3 depends upon the collision rate. If all other sources of temperature dependence of k_3 are ignored, E_2 is about 6.5 kcal./mole, with an uncertainty of several kcal. The activation energy required for decomposition of thermalized *tert*-butoxy is twice this value.[20,24]

The constant k_2 was estimated to be $\leqq 8 \times 10^9$ sec.$^{-1}$. If E_2 is 6.5 kcal., $A_2 \leqq 10^{14.7}$ sec.$^{-1}$. If reaction 3 goes in one collision in one hundred, A_2 is reduced to a value near the middle of the range expected for a simple unimolecular reaction.

(e) **Effect of Wave Length.**—The lowered quantum yield of acetone, ~0.2, when 3130 Å. radiation is used, compared with ~0.8 at λ 2537 Å., demonstrates the strong effect of wave length. Thompson and Dainton[7] found that prolonged illumination of *tert*-butyl nitrite vapor in the banded region led to no net decomposition. This suggests that the excited radical effect must be indeed small under these conditions.

ADDED IN PROOF.—The ratio k_1/k_2 for moderation of excited radicals by ethane has been found to be 6×10^{20} ml./molecule at 3130 Å., a value substantially greater than that found at 2537 Å. (Table II). The effect of a change in wave length is therefore to change both the number and energy of the excited radicals formed in the primary process.

Conclusions.—The present results indicate that an excited radical effect must be considered in the vapor-phase photolysis of alkyl nitrites following absorption of light in the continuum. The apparent occurrence of deactivation processes suggests that the effect may be much less important in the liquid phase.

It is not possible to decide with certainty in which degrees of freedom the excitation lies. Relative deactivation efficiencies given in Table II are consistent with quenching of vibrational energy, but the possibility of electronic excitation of the radicals may not be excluded.

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(23) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p. 84.

(24) D. H. Volman and W. M. Graven, *J. Am. Chem. Soc.*, **75**, 3111 (1953); G. R. McMillan, *ibid.*, **82**, 2422 (1960).

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The Photochemistry of Nitrogen Dioxide at 3130 and 4050 Å.

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RECEIVED FEBRUARY 3, 1962

In mixtures of nitrogen dioxide and O^{18}-enriched oxygen, scrambling in the O_2 and transfer of O^{18} to the NO_2 are produced by irradiation at 3130 Å., but not at 4050 Å. Added gases are more effective in quenching the nitrogen dioxide photolysis at 4050 Å. than at 3130 Å. At both wave lengths nitrogen dioxide reacts with isobutane to form *t*-nitroisobutane. The quantum yield of this reaction with 6 mm. NO_2 and 1 atm. $i\text{-}C_4H_{10}$ is ≈0.1 at 3130 Å. and ≈0.35 at 4050 Å., while that of the photolysis with 6 mm. NO_2 alone is 0.96 at 3130 Å. and 0.36 at 4050 Å. An activated molecule mechanism is capable of explaining these and other observations on nitrogen dioxide at 4050 Å.

Introduction

At 3130 and 3660 Å. the diffuse absorption spectrum, absence of fluorescence, and photochemical behavior of nitrogen dioxide long have been regarded as evidence of its photodissociation with a primary yield of close to unity. At 4050 Å. the absorption spectrum shows discrete structure and the molecule fluoresces, yet photochemical reactions also occur, with some characteristics in common and some distinctly different from those at shorter wave lengths. Both dissociation and activated molecule reactions have been postulated[1,2] as primary photochemical processes at 4050 Å., but evidence regarding the relative importance of these and the photophysical processes which also occur has been indeterminate, and hitherto no complete explanation of the photochemistry of

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(1) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941.

(2) S. Sato and R. J. Cvetanović, *Can. J. Chem.*, 36, 279 (1958).