TABLE II

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

$T = 26°, \lambda = 2537$ Å.

Deactivating gas	$10^{20}\ k_i/k_2$, 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°, $k_i/k_2 = 1.2 \times 10^{-20}$ 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_i/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.

(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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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*-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).

nitrogen dioxide at this wave length has been proposed.

Experimental data bearing on the photochemistry of nitrogen dioxide at 3130 and 4050 Å. were presented by one of the authors (T. C. H.) in a doctoral dissertation at the University of California, Los Angeles, in 1953. With the increasing importance of nitrogen dioxide photochemistry in air pollution, some of these data have been rather widely quoted.[3-7] They are here described in detail, and the mechanisms which they suggest are applied to a number of hitherto uncoördinated observations.

Experimental

Photolyses were conducted in a 3 × 20 cm. cylindrical fused silica cell connected by graded seals and stopcocks to the storage bulbs, manometers, traps, and Toepler and diffusion pumps required for introducing, measuring, and removing the desired gases. The photolysis system, which was mercury free and had a volume of 210 ml., consisted of the cell, a trap, and a solenoid circulating pump, and was isolated from the gas handling system during runs by stopcocks so placed as to minimize blind end tubes. The system was enclosed in an insulated box for temperature control, and most runs were conducted at 25°. For higher temperatures the box was heated by electric coils and a circulating fan.

The cell was illuminated along its axis by a collimated and filtered light beam from a Hanovia Type A medium pressure mercury arc, which was housed in a separate box. Two filters were used: (1) a 3-cm. layer of 46 g. of $NiSO_4 \cdot 6H_2O$ and 14 g. of $CoSO_4 \cdot 7H_2O$ in 100 cc. of H_2O plus a 1-cm. layer of 5 g. of KH phthalate/l. H_2O, and (2) a 3-cm. layer of 0.02 *N* I_2 in CCl_4 plus a 1-cm. layer of 0.05% quinine hydrochloride in H_2O. With the first filter the phthalate solution was constantly renewed by circulation from a 5-l. reservoir, and the decay in transmission was less than 1% over a 5-hr. irradiation. From the transmission curves of the filters, measured on a Cary spectrophotometer, and the line intensities of the arc, it was estimated that 94% of the radiation transmitted by filter 1 was at 3130 Å. and 88% of that transmitted by filter 2 was at 4047–4078 Å.

Energy flux measurements before, during, and after each photolysis were made with a phototube, calibrated *in situ* against a thermopile-galvanometer system which in turn was calibrated against standard carbon lamps. By means of auxiliary illumination from a small incandescent lamp, the phototube also served as a photometer for measuring the NO_2 concentration in the cell before and after each run.

Nitrogen dioxide was purified by the method of Harris, *et al.*,[8] and stored at −80° as white solid N_2O_4. Carbon dioxide, difluorodichloromethane, and the hydrocarbons used as added gases were purified by freezing, pumping, and volatilizing the middle third of each sample.

In the standard photolysis procedure, after the system had been thoroughly outgassed and the mercury arc brought to operating equilibrium, stopcocks leading to the Toepler pump and manometer were closed to prevent contact between liquid mercury and NO_2. The N_2O_4 storage bulb then was warmed, NO_2 was introduced to the desired pressure as measured by the photometer, and any foreign gas to be used was added. The system contents then were condensed at liquid nitrogen temperature in the trap, the system pumped, the contents volatilized and recondensed, and the system repumped. Next the radiation flux was measured, the trap contents revolatilized, the solenoid pump activated, the NO_2 pressure measured by photometry and the irradiation started. Transmitted radiation was measured at the beginning and end of the run.

After the run, the remaining NO_2 pressure was read by photometry, the condensable products again frozen out, and the radiation flux remeasured. The non-condensable products then were collected by Toepler pump in the thimble of a Blacet–Leighton microgas analysis apparatus, the volume measured, and the sample analyzed by transfer of a small portion to a modified Westinghouse Type LV mass spectrometer. The oxygen content was determined from the mass 32 peak height relative to that from pure air, and from this and the radiation measurements the quantum yield was calculated by the standard method.[9]

In the runs with O^{18}-enriched O_2, the sample was stored over mercury in a fused silica thimble of the microgas analysis apparatus, from which the desired amount could be drawn through a capillary for introduction into either the photolysis system or the mass spectrometer. As originally received, most of the O^{18} in the sample was present as $O^{18}O^{16}$. It was equilibrated before use by irradiation, in the thimble, by 2537 Å. from a resonance lamp. A 1-hr. irradiation gave complete equilibration but resulted in a slight sacrifice in O^{18}-content, probably due to outgassing of $O^{16}O^{16}$ from the walls.

All quantum yield runs were conducted at an initial NO_2 pressure of ≈6 mm., and irradiation times, ranging from a few minutes to an hour or more, were chosen to keep the amount of NO_2 decomposition small, generally ≈5% of that initially present.

Results

The results from the irradiation of mixtures of NO_2 and O^{18}-enriched O_2 are summarized in Table I. In these experiments, the initial NO_2 pressures were adjusted to give approximately the same amounts of photodecomposition at the two wave lengths. After irradiation, the mixture was refrigerated at −190° for 30 min. to remove the oxides of nitrogen, and the amount and distribution of the O^{18} in the oxygen was determined by mass spectrometry. The experiments were conducted at 25°, and a dark run of 12 hr. at 115° showed no exchange.

TABLE I

SUMMARY OF ISOTOPE EXCHANGE DATA

	Irradiated at	
	3130 Å.	4047 Å.
Initial NO_2 pressure, mm.	1.0	4.6
O^{18}-enriched O_2 pressure, mm.	0.344	0.281
Photoproduced O_2 pressure, mm.	0.257	0.291
Atom % O^{18} in O_2 before irradiation	24.5	24.5
Atom % O^{18} in O_2 after irradiation[a]	14.0	25.1
Estimated atom % O^{18} in $NO + NO_2$ after irradiation	4.8	0.0
Ratio O_2^{36}/O_2^{34} before irradiation	0.159	.159
Ratio O_2^{36}/O_2^{34} after irradiation	.076	.148

[a] Corrected for photoproduced O_2 (mass 32).

The results at 3130 Å. show two effects, a loss of O^{18} in the oxygen and a reduction in the O_2^{36}/O_2^{34} ratio after irradiation. The loss of O^{18} presumably was due to its transfer to the remaining NO and NO_2, and confirming this, mass spectrographic examination of the remaining NO_2 showed a small peak at mass 48 accompanying the major peak at mass 46. Both of these effects would be expected to follow photodissociation of the NO_2 to yield single O^{16} atoms. In contrast, irradiation at 4050 Å. produced no significant change in the

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(3) H. W. Ford, *Can. J. Chem.*, **38**, 1780 (1960).

(4) H. W. Ford and H. Endow, *J. Chem. Phys.*, **27**, 1156, 1277 (1957).

(5) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, Inc., New York, N. Y., 1961.

(6) P. A. Leighton and W. A. Perkins, Jr., "Solar Radiation, Absorption Rates, and Photochemical Primary Processes in Urban Air," Air Pollution Foundation, Report No. 14, Los Angeles, California, 1956.

(7) P. A. Leighton and W. A. Perkins, Jr., "Photochemical Secondary Reactions in Urban Air," Air Pollution Foundation, Report No. 24, San Marino, California, 1958.

(8) L. Harris, G. W. King, W. S. Benedict and R. W. B. Pearse, *J. Chem. Phys.*, **8**, 765 (1940).

(9) P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, **54**, 3165 (1932).

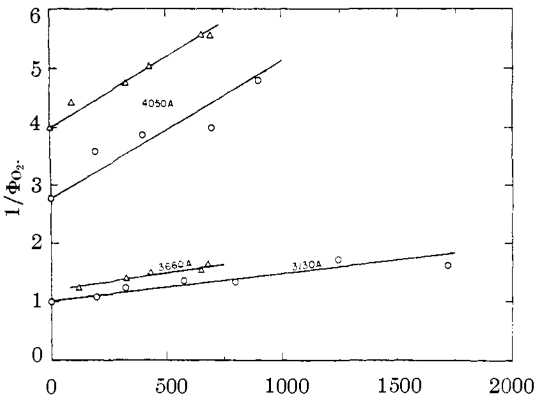

Fig. 1.—Effect of carbon dioxide on quantum yield of oxygen formation: ⊙, this work; △, Holmes and Daniels.[10]

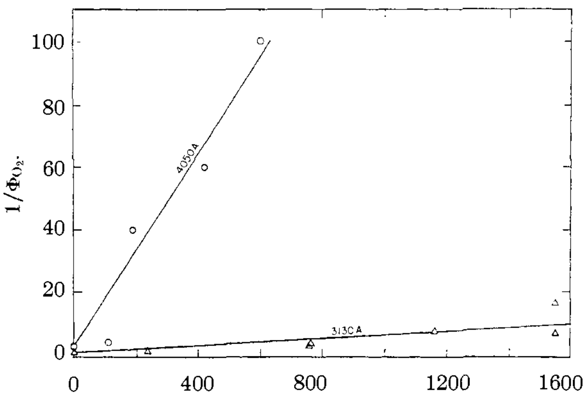

Fig. 2.—Effect of difluorodichloromethane on quantum yield of oxygen formation.

O_2^{36}/O_2^{34} ratio and no significant transfer of O^{18} from the oxygen to the nitrogen dioxide.

The quantum yields obtained for oxygen formation from pure NO_2 at 25° and ≈6 mm. pressure where $\Phi_{O_2} = 0.96$ at 3130 Å. and $\Phi_{O_2} = 0.36$ at 4050 Å. One run at 147° and 4050 Å. gave $\Phi_{O_2} = 0.37$, indicating that the yield at this wave length is temperature independent or nearly so.

The effects of added carbon dioxide and difluorodichloromethane on the quantum yields are shown in Fig. 1 and 2. In neither case were any observable products of interaction with the added gases obtained, and at both wave lengths the yields were approximately inversely proportional to the added gas pressure. The straight lines in the figures give the values in Table II for b in $1/\Phi_{O_2} = a + b(M)$. The effects of ethane and propane on Φ_{O_2} were measured at 3130 Å. with similar results, and the observed coefficients are included in Table II. All runs were at $P_{NO_2} \approx 6$ mm.

Both in nitrogen dioxide alone and in the presence of added gases the quantum yield at 3130 Å. decreased with decreasing NO_2 pressure. Thus in NO_2 alone Φ_{O_2} decreased from 0.96 at $P_{NO_2} = 6$ mm. to 0.72 at $P_{NO_2} = 1.7$ mm., and in the presence of 1 atm. of propane it decreased from 0.34 at $P_{NO_2} = 6$ mm. to ≈0.15 at $P_{NO_2} = 1.5$ mm. The effects of decreasing NO_2 pressure were not studied at 4050 Å.

TABLE II

QUENCHING COEFFICIENTS FOR EFFECTS OF ADDED GASES ON Φ_{O_2}

Added gas, M	Wave length, Å.	b, l. mole^{-1}
CO_2	3130	8.2
CO_2	4050	43
CF_2Cl_2	3130	100
CF_2Cl_2	4050	2800
C_2H_4	3130	33
C_3H_8	3130	46
i-C_4H_{10}	3130	165

In the case of isobutane a photochemical interaction occurred, both at 3130 and 4050 Å. A condensable product was obtained which remained in the trap when the nitrogen oxides and unreacted hydrocarbon had been pumped off at −80°. Application of the techniques of Rock[11] and Thomas and Sigfried[12] suggested that the bulk of this condensate was tertiary nitroisobutane, and comparison of its mass spectrogram with those of a number of possible compounds showed a close resemblance only with that of t-nitroisobutane. The same product was obtained thermally by heating a mixture of 6 mm. of NO_2 and 1 atm. of isobutane at 130° for 1 hr. In both the photochemical and thermal reactions, water also was identified as a product. The composition of the condensable product, as shown by its mass spectrogram, was essentially independent of the NO_2 and isobutane pressure over a wide range.

The quantum yields in Table III were based on the height of the mass 56 peak in the spectrogram of the condensate, relative to that from a known quantity of t-nitroisobutane added to a NO_2–isobutane mixture in the photolysis system, then condensed and separated by the same procedure. The peak heights so obtained averaged only 0.76 of those given by introducing the same quantity of t-nitroisobutane directly into the spectrometer system, showing that the procedure used did not give complete recovery. The variability in yield shown by the runs at 3130 Å. and ≈1 atm. of isobutane (Table III) probably also is due to incomplete recovery, and for this reason the results are only semi-quantitative. The most that may be said is that the yield at 3130 Å. is approxi-

TABLE III

QUANTUM YIELD OF t-ISONITROBUTANE FORMATION

$T = 25°$, $P_{NO_2} = 6 \pm 0.3$ mm.

Wave length, Å.	Isobutane pressure, mm.	$\Phi_{t\text{-}C_4H_9NO_2}$
3130	756	0.12
	756	.05
	768	.08
	774	.14
	1206	.08
4050	384	.16
	756	.35

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[10] H. H. Holmes and F. Daniels, *J. Am. Chem. Soc.*, **56**, 630 (1934).

[11] S. M. Rock, *Anal. Chem.*, **23**, 261 (1951).

[12] B. W. Thomas and W. D. Sigfried, *ibid.*, **21**, 1022 (1949)

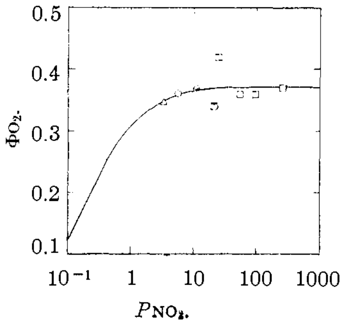

Fig. 3.—Quantum yields of oxygen formation in nitrogen dioxide photolysis at 4050 Å.: ⊙, this work; △, Dickinson and Baxter[13]; □, Norrish.[14]

mately 0.1 at isobutane pressures of 750–1200 mm., while the yield at 4050 Å. may be higher than that at 3130 Å. and may be proportional to the isobutane pressure.

Discussion

The isotope exchange experiments give direct evidence of the photodissociation of nitrogen dioxide at 3130 but not at 4050 Å., supporting the earlier assumptions that this is the case.[1,3,5] Reactions following dissociation have been discussed in detail by Ford,[3] with the conclusion that the mechanism which best conforms with present understanding, under conditions such that the reactions of O atoms with NO and O_2 are negligible, is

$$NO_2 + h\nu \longrightarrow NO + O \qquad I \quad (1)$$
$$O + NO_2 \longrightarrow NO + O_2 \qquad k_2 \quad (2)$$
$$O + NO_2 \longrightarrow NO_3' \qquad k_3 \quad (3)$$
$$NO_3' \longrightarrow NO_2 + O \qquad k_4 \quad (4)$$
$$NO_3' + NO_2 \longrightarrow NO_2 + O_2 + NO \qquad k_5 \quad (5)$$
$$NO_3' + M \longrightarrow NO_3 + M \qquad k_6 \quad (6)$$
$$NO + NO_3 \longrightarrow 2NO_2 \qquad (7)$$

For the quantum yield of oxygen formation this gives

$$\frac{1}{\Phi_{O2}} = 1 + \frac{k_3k_6(M)}{k_2k_4 + (k_2 + k_3)k_5(NO_2) + k_2k_6(M)} \qquad (8)$$

Introducing Ford and Endow's value[4] of $k_2 = 2.1 \times 10^9$ l. mole^{-1} sec.$^{-1}$ and Ford's estimate of $k_3 \approx 5 \times 10^{11}$, the observed reduction in Φ_{O2} with decreasing NO_2 pressure in the presence of 1 atm. of C_3H_8 gives $k_4/k_5 \approx 0.01$ mole l.$^{-1}$, and the data in Table II yield the ratios

M =	CO_2	CF_2Cl_2	C_2H_4	C_3H_8	$i\text{-}C_4H_{10}$
k_6/k_5 =	0.003	0.038	0.013	0.017	0.06

The Ford mechanism predicts a Φ_{O_2} of unity for the nitrogen dioxide photolysis at 3130 Å. in the absence of added gases. A value of less than unity might be due to a primary dissociation yield of less than unity, to the participation of NO_2 as M in reaction 6, to other reactions such as $NO + NO_3' \rightarrow 2NO_2$, or to the wall removal of O atoms or NO_3'. Of these possibilities, only wall removal will explain the observed decrease in Φ_{O_2} with decreasing NO_2 pressure in the absence of added gases. Insertion of a wall removal term $k_w(NO_2)^{-1}$ in eq. 8, with $k_w = 2.45 \times 10^3$ sec.$^{-2}$, accounts for the observed values of $\Phi_{O_2} = 0.96$ at $P_{NO_2} = 6$ mm. and 0.72 at $P_{NO_2} = 1.7$ mm. quite precisely. This explanation supports a primary yield of unity and requires that, for M = NO_2, $k_6/k_5 < 0.04$.

At 4050 Å. the exchange experiments indicate that NO_2 is not photodissociated in significant amounts. If so, its photoreactions at this wave length must involve activated molecules, and these processes must account for the experimental observations on the quantum yield of NO_2 photolysis, on its fluorescence, and on its reactions with hydrocarbons.

A mechanism which appears to accomplish this for the photolysis and fluorescence is

$$NO_2 + h\nu \longrightarrow NO_2' \qquad I_a \quad (9)$$
$$NO_2' + NO_2 \longrightarrow 2NO + O_2 \qquad k_{10} \quad (10)$$
$$NO_2' + NO_2 \longrightarrow NO_2 + NO_2 \qquad k_{11} \quad (11)$$
$$NO_2' + M \longrightarrow NO_2 + M \qquad k_{12} \quad (12)$$
$$NO_2' \longrightarrow NO_2 + h\nu \qquad k_{13} \quad (13)$$
$$NO_2' \longrightarrow NO_2'' \qquad k_{14} \quad (14)$$
$$NO_2'' \longrightarrow NO_2 + h\nu'' \qquad k_{15} \quad (15)$$
$$NO_2'' + NO_2 \longrightarrow NO_2 + NO_2 \qquad k_{16} \quad (16)$$
$$NO_2'' + M \longrightarrow NO_2 + M \qquad k_{17} \quad (17)$$

For the quantum yield of oxygen formation this gives

$$\frac{1}{\Phi_{O_2}} = 1 + \frac{k_{11}}{k_{10}} + \frac{k_{13} + k_{14}}{k_{14}(NO_2)} + \frac{k_{12}(M)}{k_{10}(NO_2)} \qquad (18)$$

In pure NO_2 the mechanism thus predicts that at pressures such that $k_{10}(NO_2) > k_{13} + k_{14}$ the quantum yield will approach independence of the pressure with a limiting value of $1/\Phi_{O_2} = 1 + k_{11}/k_{10}$. A fit with reported values at 4050 Å. is shown in Fig. 3, where the line is from eq. 18 with (M) = 0 and

$$\frac{k_{11}}{k_{10}} = 1.7, \frac{k_{13} + k_{14}}{k_{10}} = 3 \times 10^{-5} \text{ mole l.}^{-1} \qquad (19)$$

At low nitrogen dioxide pressures the mechanism predicts that Φ_{O_2} will fall off and approach proportionality to the pressure, but it is apparent from Fig. 3 that no observations are available in the proper range to test this. Values of the ratio $(k_{13} + k_{14})/k_{10}$ much larger than 3×10^{-5} mole l.$^{-1}$ produce significant departures from the observed yields at 3–11 mm., but smaller values of this ratio, with some adjustment in k_{11}/k_{10}, give equally good fits. A value of $(k_{13} + k_{14})/k_{10}$ much smaller than 3×10^{-5} may, however, be questioned on the basis of absolute rates. Thus, from the absorption coefficients of nitrogen dioxide, Neuberger and Duncan[15] have estimated a lifetime relative to radiative transition of 2.6×10^{-7} sec. for NO_2', which gives $k_{13} = 3 \times 10^6$ sec.$^{-1}$. Even with $(k_{13} + k_{14})/k_{10} = 3 \times 10^{-5}$ this requires that $k_{10} > 10^{11}$ l. mole^{-1} sec.$^{-1}$, and to explain the observed values of Φ_{O_2}, k_{11} must be larger still.

With added carbon dioxide and difluorodichloromethane, the values of *b* in Table II, combined with eq. 18 and 19 for $P_{NO2} = 6$ mm. yield the ratios

M =	CO_2	CF_2Cl_2
k_{12}/k_{10} =	0.014	0.9

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(13) R. G. Dickinson and W. P. Baxter, *J. Am. Chem. Soc.*, **50**, 774 (1928).

(14) R. G. W. Norrish, *J. Chem. Soc.*, 1158 (1929).

(15) D. Neuberger and A. B. F. Duncan, *J. Chem. Phys.*, **22**, 1693 (1954).

Compared with these ratios, that of $k_{11}/k_{10} = 1.7$ indicates that reaction 11 is faster than would be expected if only simple deactivation were involved. An alternate path which might account for this is

$$NO_2' + NO_2 \longrightarrow NO_3 + NO \qquad (11a)$$

followed by (7). This conforms with Ford's suggestion that O, NO_2', and NO_3' may each attack NO_2 by two paths, to form either a peroxy or a non-peroxy activated complex. The peroxy complex in each case in postulated to yield OONO, which decomposes to O_2 + NO, while the non-peroxy complex yields NO_3. Table IV lists the reactions involved and the peroxy/non-peroxy rate constant ratios indicated by Ford's estimates and this work. The apparent increase in this ratio in going from O atoms to NO_3' is noteworthy.

TABLE IV

REACTIONS OF O, NO_2', AND NO_3' WITH NO_2

Reactants	Reaction no. of process forming Peroxy complex	Reaction no. of process forming Non-peroxy complex	Rate constant ratio $\frac{\text{Peroxy}}{\text{Non-peroxy}}$
$O + NO_2$	2	3	0.004
$NO_2' + NO_2$	10	11a	0.6
$NO_3' + NO_2$	5	$6(M = NO_2)$	>25

The greater effects of added gases on Φ_{O_2} at 4050 relative to 3130 Å. are reflected in the larger ratios of k_{12}/k_{10} relative to k_6/k_5. The difference thus may be assigned to the postulate that, relative to their collisional deactivations, the reaction of NO_2' with NO_2 to form a peroxy complex is less efficient than that of NO_3' with NO_2.

The radiationless transfer (14) was proposed by Neuberger and Duncan[15] to account for their observations on the fluorescence of nitrogen dioxide. On excitation by blue light, at NO_2 pressures of 0.6 to 12 μ, the fluorescence gave lifetime traces yielding the relation, with P_{NO_2} in mm.

$$1/t_f = 2.25 \times 10^4 + 2 \times 10^6\ P \text{ sec.}^{-1} \qquad (20)$$

Exciting bands centered at 3950, 4300, and 4650 Å. gave approximately the same values of t_{f_0}. On excitation by 5460 Å., on the other hand, the fluorescence gave no observable lifetime trace. This led Neuberger and Duncan to postulate that the first excited state NO_2' is short lived and the fluorescence excited by 5460 Å. comes only from this state, while the second state NO_2'' is relatively long lived and produced the traces observed at 3950–4650 Å. The first state, NO_2', also might fluoresce at 3950–4650 Å. but the experimental method used would permit no decision on this.

For the fluorescent lifetime of NO_2'' the mechanism gives

$$1/t_f'' = k_{15} + k_{16}(NO_2) + k_1\ (M) \qquad (21)$$

From Neuberger and Duncan's data $k_{15} = 2.25 \times 10^4$ sec.$^{-1}$ and $k_{16} = 3.7 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$. The absence of any observed wave length variation in t_f over the range 3950–4650 Å. suggests that, over this range at least, k_{15} and k_{16} are independent of the exciting wave length.

The quantum yields of fluorescence derived from the mechanism are

$$\Phi_f' = \frac{k_{13}}{k_{13} + k_{14} + (k_{10} + k_{11})(NO_2) + k_{12}(M)} \qquad (22)$$

$$\Phi_f'' = \frac{k_{14}k_{15}}{[k_{13} + k_{14} + (k_{10} + k_{11})(NO_2) + k_{12}(M)][k_{15} + k_{16}(NO_2) + k_{17}(M)]} \qquad (23)$$

These equations show that, with increasing (NO_2) or increasing (M), the fluorescence from NO_2'' will be quenched more rapidly than that from NO_2'. The predicted quenching curves for pure NO_2 in Fig. 4 are based on the rate constant ratios in (19) and are independent of the absolute values of Φ_{f_0}. They suggest that, if NO_2 does fluoresce from both states at 4050 Å. at pressures above ≈0.1 mm. most of that observed will be from NO_2'.

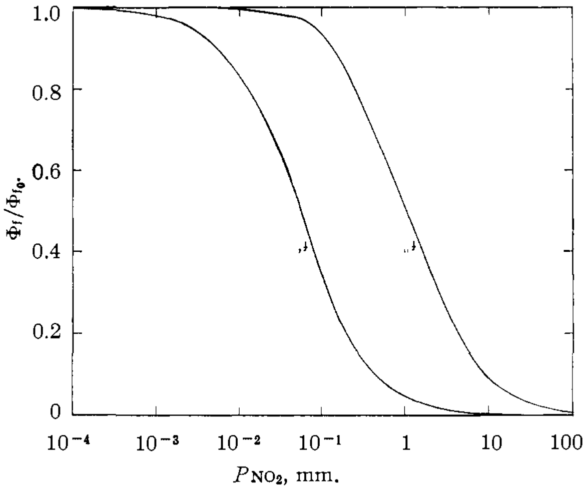

Fig. 4.—Predicted quenching of nitrogen dioxide fluorescence at 4050 Å.

Norrish[16] reported a weakening of the fluorescence in the region of 6250–6550 Å., while that in the range of 5600–6050 Å. was little affected, in going from 4350 to 4050 Å. as the exciting wave length. This change in distribution was not confirmed by Neuberger and Duncan. Some weakening of fluorescence in going from 4350 to 4050 Å. might be expected from eq. 22 and 23, since k_{10} is essentially zero at the longer wave length. If the value of k_{10} at 4050 Å. is that given by (19) and the other constants do not change with wave length, $\Phi_{f(4050)}/\Phi_{f(4350)}$ would be 0.88 at P_{NO_2} = 0.1 mm. and 0.64 at P_{NO_2} = 10 mm. An increase in k_{14} with decreasing wave length would increase $\Phi_{f''}$ but decrease $\Phi_{f'}$ and in the case, if fluorescence occurs from both states, the over-all effect observed would depend on the pressure.

In mixtures of NO_2, N_2O_4, and N_2O_5 exposed to light at 4050 Å. and shorter wave lengths the only observed change is the decomposition $N_2O_5 \rightarrow 2NO_2 + {}^1/_2\ O_2$, accompanied by the association $2NO_2 \rightleftarrows N_2O_4$. The concentration of the light absorber NO_2 increases as the reaction proceeds. Using a constant pressure of 51.5 mm. of N_2O_5 at 0°, Holmes and Daniels[10] estimated the quantum yields of N_2O_5 decomposition from the total product pressure and the equilibrium constant $P^2_{NO_2}/P_{N_2O_4} = 13.53$, with P in mm. At the two wave

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[16] G. W. Norrish, *J. Chem. Soc.*, 1611 (1929).

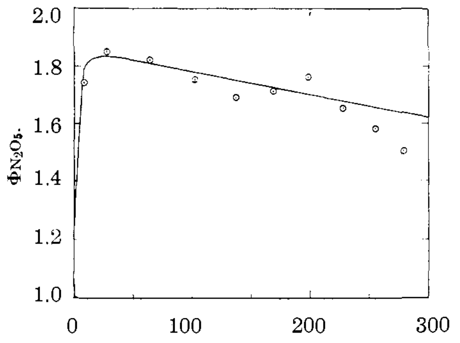

Fig. 5.—Quantum yields in the photolysis of nitrogen pentoxide at 3660 Å.

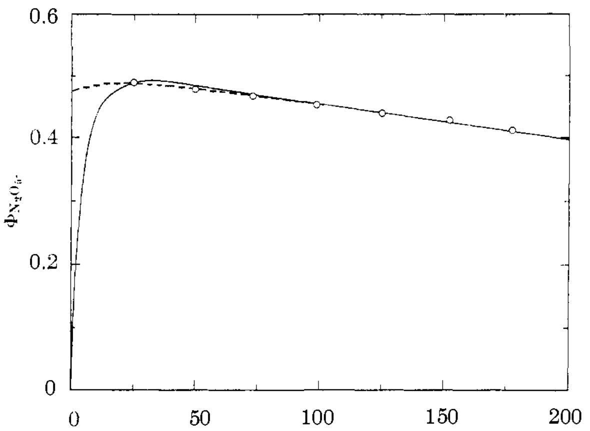

Fig. 6.—Quantum yields in the photolysis of nitrogen pentoxide at 4050 Å.

lengths studied in the NO_2 photodissociation region, 3130 and 3660 Å., under these conditions it is necessary in estimating the yields relative to NO_2 absorption to correct for absorption by N_2O_4, and at 3130 Å. this correction is quite severe. Using Holmes and Daniels[10] absorption coefficients for NO_2 and N_2O_4, the estimated yields at 3130 Å. are somewhat larger, while using Hall and Blacet's coefficients,[17] they are smaller than those at 3660 Å. For this reason it is believed that there is no significant difference in the yields relative to NO_2 absorption at the two wave lengths, and those at 3660 Å. are probably the more reliable.

These values are plotted as circles in Fig. 5 against the mean product pressure during each time interval over which Φ was measured. They may be explained by reactions 1–7 together with $N_2O_5 \rightarrow NO_3 + NO_2$. The line in Fig. 5 is estimated from eq. 8 with $\Phi_{N_2O_5} = 2\Phi_{O_2}$, k_2, k_3, and k_4/k_5 as before, and $k_6/k_5 = 0.003$ for $M = NO_2$ and O_2, 0.01 for $M = N_2O_5$, and 0.06 for $M = N_2O_4$.

Similarly, Holmes and Daniels' results at 4050 Å. shown as circles in Fig. 6, may be explained by reactions 9–14, together with $N_2O_5 \rightarrow NO_3 + NO_2$ and (7). The solid line in Fig. 6 is from eq. 18, with the ratios in (19) and $k_{12}/k_{10} = 0.14$ for $M = N_2O_5$, 0.7 for $M = N_2O_4$, and 0.014 for $M = O_2$.

These explanations may be questioned on at least two points. First, they require the assumption that k_6 and k_{12} are smaller for $M = N_2O_5$ than for $M = N_2O_4$. Second, the mechanism at 4050 Å. predicts a quantum yield of zero at zero product pressure, whereas Holmes and Daniels' results suggest a finite value at zero pressure. These points suggest the possibility of direct reactions of NO_3' and NO_2' with N_2O_5, such as

$$NO_3' + N_2O_5 \longrightarrow NO_2 + O_2 + 2NO_2 \qquad (24)$$

$$NO_2' + N_2O_5 \longrightarrow NO + O_2 + 2NO_2 \qquad (25)$$

For example, adding (25) to the preceding mechanism for 4050 Å. gives

$$\frac{2}{\Phi_{N_2O_5}} = \frac{1}{\Phi_{O_2}} = 1 + \frac{k_{13} + k_{14} + k_{11}(NO_2) + k_{12}(M)}{k_{10}(NO_2) + k_{25}(N_2O_5)} \qquad (26)$$

The dashed line in Fig. 6 is from this equation with $k_{25}/k_{10} = 1$ and $k_{12}/k_{10} = 3.2$ for $M = N_2O_5$, 1.2 for $M = N_2O_4$. It should be emphasized that these values are only illustrative, other combinations give equally good or even better fits, and an experimental determination of the intercept at $P = 0$ is required for any definite specification.

The photoreaction of nitrogen dioxide with isobutane at 3130 Å. probably involves abstraction of the tertiary hydrogen by oxygen atoms and hydroxyl radicals, and combination of the resultant isobutyl radicals with NO_2 to give nitroisobutane

$$O + i\text{-}C_4H_{10} \longrightarrow OH + i\text{-}C_4H_9 \quad k_{27} \qquad (27)$$

$$OH + i\text{-}C_4H_{10} \longrightarrow H_2O + i\text{-}C_4H_9 \qquad (28)$$

$$i\text{-}C_4H_9 + NO_2 \longrightarrow t\text{-}C_4H_9NO_2 \qquad (29)$$

Together with reactions 1–6 these give, as an upper limit since other reactions of OH and i-C_4H_9 radicals are not taken into account

$$\frac{2}{\Phi_{C_4H_9NO_2}} = 1 + \frac{k_2(NO_2)}{k_{27}(C_4H_{10})} + \frac{k_3(NO_2)[k_5(NO_2) + k_6(M)]}{k_{27}(C_4H_{10})[k_4 + k_5(NO_2) + k_6(M)]} \qquad (30)$$

Based on Cvetanovič's results[18] the value of k_{27} may be estimated at $\approx 5 \times 10^7$ l. mole^{-1} sec.$^{-1}$. With this and the estimates of k_2, k_3, k_4/k_5, and k_6/k_5 derived from the NO_2 photolysis, for $M = i$-C_4H_{10} and 6 mm. of NO_2 eq. 30 gives $\Phi_{C_4H_9NO_2} \approx 0.11$ and 0.12 for 760 and 1200 mm. of i-C_4H_{10}. These are consonant with the experimental conclusion that $\Phi_{C_4H_9NO_2} \approx 0.1$ in this pressure range.

The approach of the yield at 3130 Å. to independence of isobutane pressure, which the mechanism predicts and the experimental data do not deny, results from the coincidence that at the pressures used $k_2(NO_2) < k_{27}(C_4H_{10}) < k_3(NO_2)$ and $k_5(NO_2) < k_6(M) < k_4$. At higher NO_2 pressures, or either higher or lower i-C_4H_{10} pressures, a greater change in yield with isobutane pressure is to be expected.

At 4050 Å. the explanation of the nitrogen dioxide-isobutane reaction must be sought in terms of activated molecules. A postulated mechanism is

$$NO_2' + i\text{-}C_4H_{10} \longrightarrow HNO_2 + i\text{-}C_4H_9 \quad k_{31} \qquad (31)$$

$$i\text{-}C_4H_9 + NO_2 \longrightarrow i\text{-}C_4H_9NO_2 \qquad (29)$$

$$2HNO_2 \longrightarrow H_2O + NO + NO_2 \qquad (32)$$

Combining these with reactions 9–14 introducing the rate constant ratios in (19), and neglecting

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(17) T. C. Hall and F. E. Blacet, *J. Chem. Phys.*, **20**, 1745 (1952).

(18) R. J. Cvetanovič, *ibid.*, **30**, 19 (1959).

the resultant small term containing $k_{13} + k_{14}$ gives, for 4050 Å.

$$\frac{1}{\Phi_{C_4H_9NO_2}} = 1 + \frac{k_{12}}{k_{31}} + \frac{2.7k_{10}(NO_2)}{k_{31}(C_4H_{10})} \tag{33}$$

In this case the variation in quantum yield with isobutane pressure, or with the $(NO_2)/(C_4H_{10})$ ratio, is more straightforward than that predicted at 3130 Å. The dependence on pressure indicated by the yields in Table III suggests that, when M = i-C_4H_{10}, k_{12}/k_{13} is small, and the absolute yields suggest that $k_{10}/k_{31} \approx 10^2$, but the experimental values are so rough that this cannot be stated with certainty. To a first approximation, the yield at 4050 Å. will exceed that at 3130 Å. if $2.7k_{10}/k_{31} < k_3k_6(M)/2k_{27}k_4$, and in the investigated pressure range this would appear to be the case. The postulated mechanisms thus permit both a higher yield and a greater dependence on isobutane pressure at 4050 relative to 3130 Å.

The observations of Sato and Cvetanović[2] on the photoöxidation of 1-butene by nitrogen dioxide, where again the major products were identical but the product yields at 4050 Å. appeared to equal or exceed those at shorter wave lengths, may be explained by postulating that O atoms and NO_2' react with 1-butene to yield the same first product

$$3130\ \text{Å}.:\ O + C_4H_8 \longrightarrow C_4H_8O \quad k_{34} \tag{34}$$

$$4050\ \text{Å}.:\ NO_2' + C_4H_8 \longrightarrow NO + C_4H_8O \quad k_{35} \tag{35}$$

The resulting quantum yield equations will resemble (30) and (33), with appropriate substitutions and elimination of the factor 2 in (30). Cvetanović's value of k_{34} is 1.1 × 10^9 l. mole^{-1} sec.$^{-1}$ and the pressures used by Sato and Cvetanović were 3 mm. of NO_2 and 30 mm. of i-C_4H_8. For these values eq. 30 properly revised gives $\Phi_{34} = 0.45$. The yield at 4050 Å. and the same pressures will exceed this value if $(k_{12} + 0.27k_{10})/k_{35} < 1.2$.

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[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CAN.]

The Photo-oxidation of Azoethane[1]

BY H. CERFONTAIN[2] AND K. O. KUTSCHKE

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The photo-oxidation of azoethane has been studied over the temperature range 28° to 152° at various oxygen and azoethane pressures and over a wide range of intensities. Nitrogen, acetaldehyde and ethanol are major products at all temperatures. The amount of nitrogen formed is greater than in the photolysis of azoethane in the absence of oxygen and increases with decreasing oxygen pressure within given limits, especially at high temperatures, where nitrous oxide and ethylene become important products. A mechanism for the formation of ethylene, nitrous oxide and additional nitrogen is proposed. At temperatures above 100° acetaldehyde is produced, in part, by oxidation of ethoxy radicals. At high conversion several C_1-products are formed. The acetyl radical is an intermediate in the formation of these products from acetaldehyde. It was not possible to determine a rate constant for the reaction of ethyl radicals with oxygen.

Introduction

In the photolysis of azoethane no evidence was found for the existence of $C_2H_5N_2$ radicals.[3] Azoethane was therefore expected to be a convenient source of ethyl radicals for a study of the reaction between these radicals and molecular oxygen.

The oxidation of ethyl radicals has been the subject of several investigations. Jones and Bates[4] have studied the photo-oxidation of ethyl iodide. They followed the course of the reaction manometrically, and concluded that acetaldehyde and ethanol are the main products. Finkelstein and Noyes[5] and, later, Jolley[6] have made an extensive study of the photo-oxidation of diethyl ketone. It seems well established that ethyl, propionyl and pentanonyl radicals are involved in the oxidation. Carbon monoxide, carbon dioxide and acetaldehyde were the major products detected. No analysis was made for ethanol. Tracer experiments showed that carbon monoxide was formed solely from the carbonyl group and that a certain fraction of the carbon dioxide, especially at higher temperature, originated from the α-ethyl carbon atom.

Ethyl hydroperoxide is the major product in the mercury-photosensitized oxidation of ethane under some conditions.[7] The results show that ethyl hydroperoxide is not formed by hydrogen abstraction of the $C_2H_5O_2$ radical from the parent compound. Turner, Callear and Cvetanović, who studied the oxidation of ethyl radicals produced from mercury-photosensitized hydrogenation of ethylene arrived at the same conclusion.[8] The main reaction producing ethyl hydroperoxide was thought to be

$$C_2H_5O_2 + HO_2 \longrightarrow C_2H_5O_2H + O_2$$

Experimental

Azoethane, prepared by Merck, Sharpe and Dohme, Montreal, was redistilled and degassed several times and the middle fraction collected and stored as a liquid in a blackened tube behind a mercury cut-off. The oxygen was

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[3] H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

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[7] J. S. Watson and B. de B. Darwent, *J. Phys. Chem.*, **61**, 577 (1957).

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