ent in our measurements, and the heat capacity data show the typical sigmoid curve anticipated in the absence of anomalous behavior. The heat capacity hump and the dielectric constant anomaly previously reported by others may be attributable to the presence of water or other impurities in their preparations. This hypothesis is consistent with the preparative methods described, but cannot be tested further because of the scant analytical data provided. Although thermal analysis[14] of the NH_4F–H_2O system indicated simple eutectic behavior with a eutectic temperature of 246°K. involving the phases NH_4F and NH_4F–H_2O, more recent studies by Zaromb and Brill[15] have indicated that solid solutions exist in the water-rich region of the system. No corresponding examination of the ammonium fluoride-rich region of the phase diagram has been published.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. LII. The Nitrous Oxide–Ethane System[1]

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The ratio of nitrogen formed photochemically at about 1900 Å. in pure nitrous oxide to that formed under identical conditions in a nitrous oxide–ethane mixture is 1.4. This indicates that the primary photochemical process is probably $N_2O = N_2 + O$ and that oxygen atoms react much more rapidly with ethane than with nitrous oxide. Several products are formed including ethylene, butane, carbon monoxide, hydrogen, methane and probably ethanol and acetaldehyde. A complete elucidation of the mechanism is not possible, due to the fact that oxygen atoms seem to react more rapidly with one or more of the products than they do with ethane itself. More ethylene is formed than one would expect from the amount of butane. Due to secondary reactions which must involve the initially formed products it has not been possible to obtain precise information about the reactions of oxygen atoms and of hydroxyl radicals.

Introduction

The absorption spectrum of nitrous oxide probably consists of a continuum extending from about 3000 Å. to shorter wave lengths.[2]

The photochemistry has been studied with radiation directly absorbed by nitrous oxide[3] as well as through mercury sensitization.[4] The reaction products (at least of the unsensitized reaction) are nitrogen, oxygen and nitric oxide. Oxygen atoms must be formed in the primary process.[3b,c,d,e]

One of the great gaps in the interpretation of oxidation reactions of organic molecules lies in the behavior of hydroxyl radicals.[5] The present work was started in the hope that oxygen atoms from nitrous oxide would react with hydrocarbons, such as ethane, to give hydroxyl radicals and that the behavior of the latter could be investigated. This hope has not been realized because oxygen atoms also react rapidly with some of the reaction products. Thus the over-all reaction is complex but certain conclusions about it are possible.

Experimental

An aluminum spark, which gives several intense lines between 1850 and 1990 Å., was used as a source of radiation. The general design of the spark was similar to that developed by Wiig and Kistiakowsky.[6] The transformer has a capacity of 10.4 KVA with a 17600 v. secondary when operated on 115 v. Actually it was operated on 220 v. primary circuit with 0.032 mfd. capacity in parallel with the spark. Air jets played directly on the spark for cooling purposes and to increase steadiness of operation.

The method of focal isolation was used to obtain approximately monochromatic radiation. The change in focal length with wave length of a quartz lens 3 cm. in diameter with a focal length of about 18 cm. was used to isolate radiation of the desired wave length. The center of the lens was blocked off. A camera iris was placed between the focus and the lens and the size of opening adjusted to allow mainly light of wave length below 2000 Å. to pass. The focus was located either by a piece of canary glass (Corning No. 9750) or by a piece of glass "silvered" with mercury. A spectrogram showed that the 1850 Å. line of aluminum did enter the cell.

The portion of the glass vacuum system of the reaction cell and the nitrous oxide and ethane purification, storage and measuring system were kept as free from mercury as possible. High vacuum stopcocks, greased with Apiezon (Type N) grease separated the various parts. Pressures in this part of the system were measured with a click gage.[7] The mercury-free portion of the system was never opened to the rest of the system without at least a Dry Ice bath on a trap connecting the two parts.

Nitrous oxide (Ohio Chemical Company) was distilled between two U-tubes four times with the condensing trap at −183° while the system was continuously open to the mercury diffusion pump. Finally the nitrous oxide was distilled through a trap at −78° to a cold finger attached to a two-liter storage bulb. Only the middle third was retained. The final product showed no impurities at −183° and none not volatile at −112°.

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[1] This work was supported in part by Contract with the Office of Naval Research, United States Navy, and with the Office of Air Research, United States Air Force. Further details are available in the Ph.D. Thesis of George Castellion, University of Rochester, 1956. This material may be reproduced by or used in any way by the United States Government.

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[3] (a) J. MacDonald, *J. Chem. Soc.*, 1 (1928); (b) W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937); (c) J. Zabor and W. A. Noyes, Jr., THIS JOURNAL, **62**, 1975 (1940); (d) M. Zelikoff and L. Aschenbrand, *J. Chem. Phys.*, **22**, 1680 (1954); (e) **22**, 1685 (1954).

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[6] E. O. Wiig and G. B. Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

[7] D. F. Smith and N. W. Taylor, *ibid.*, **46**, 1393 (1924).

The ethane (Phillips Petroleum Company, Research Grade) was passed through a sintered glass disc into fuming sulfuric acid, through a column filled with potassium hydroxide pellets and dried with anhydrous magnesium perchlorate. It was finally purified by the same procedure as the nitrous oxide with a condensing temperature of −195°. No ethylene was found by attempted catalytic hydrogenation.

Commercial *n*-butane was purified by fractional distillation at low temperatures in the same manner as ethane. There were no impurities volatile at −195° and none not volatile at −78°. Ethylene was purified by distillation in the same manner as the butane. Catalytic hydrogenation indicated 97% purity. Oxygen was prepared by heating potassium permanganate.

Cylinder nitric oxide was passed through traps cooled to −183°. It contained no impurities not condensed at −215°. Hydrogen from a cylinder was purified by passage through a heated palladium thimble.

The reaction products were fractionated into several parts and analyzed as follows.

(a) Fraction not condensed at −215°. This fraction was not condensed by solid nitrogen. Special precautions were taken to avoid either adsorption or mechanical occlusion by the substrate of gases normally volatile at these temperatures. Possible gases which could be included in this fraction are the following: N_2, CO, CH_4, H_2, O_2. The fraction was analyzed by a method already described.[8] The method will not distinguish between hydrogen and oxygen, both of which will disappear in the copper–copper oxide furnace. Additional evidence from experiments with added oxygen shows that only hydrogen is present. The amount of the product which could be either hydrogen, oxygen or a mixture of both on the basis of the copper–copper oxide furnace results is plotted *versus* the nitrogen formed when identical mixtures of nitrous oxide and ethane are illuminated for varying amounts of time. Experiments were performed with similar mixtures to which varying amounts of oxygen (up to 40% of the nitrogen eventually formed) were added before the photolysis. The amount of a product which could be either hydrogen, oxygen or both resulting from the photolysis of these mixtures is plotted on the same graph. It is found that the points for the oxygen added runs fall on the same curve which connects the points for runs with no oxygen added. Thus the product which cannot be distinguished as hydrogen, oxygen or both by the copper–copper oxide furnace is solely hydrogen. This does not mean the oxygen may not be formed in the photolysis, but rather that if it is, it is being used up so fast that its steady state concentration is very small.

Nitrogen and methane are unaffected when the furnace is maintained at 210°. Carbon monoxide is oxidized to carbon dioxide, hydrogen to water, and oxygen is converted to cupric oxide. The distinction between nitrogen and methane was made by oxidizing the latter over a heated platinum wire.

(b) Fraction volatile at −183° (liquid oxygen) but not volatile at −215°. This fraction consisted of ethane and ethylene. Since ethane was one of the principal gases used, its effect on the determination of ethylene was carefully investigated. Actually both nitrous oxide and ethane in large amounts reduced the rate of condensation of ethylene. Special precautions were necessary for adequate separation of the ethylene, and it was determined by the hydrogenation method of Shepp and Kutschke.[9]

(c) Fraction volatile at −112° but not volatile at −160°. This fraction contained large amounts of nitrous oxide and some organic compounds, apparently mainly butane. The nitrous oxide is decomposed by a very hot platinum wire at the same time that the organic compounds are oxidized to carbon dioxide and water. Nitrogen dioxide (which might result from nitrous oxide decomposition on the hot platinum wire) was caused to react with mercury to give mercuric oxide and nitric oxide. Blanks with mixtures of nitrous oxide, ethane, ethylene and butane showed the separation and analysis of butane by measurement of carbon dioxide produced from it was satisfactory. Actually mass spectrometer results showed that butane was the major product in this fraction since there appeared to be only mass peaks for butane and nitrous oxide. Small amounts of other compounds might escape detection.

(d) Fraction volatile at room temperature but not volatile at −112°. This fraction can contain several organic compounds as well as water. The carbon content was determined by combustion over a hot platinum wire in the presence of added oxygen. Water could result either from the reactions under investigation or from the combustion of organic material over the hot wire. The amounts of water proved to be too small to determine accurately by the boron hydride method.[10] No other method proved to be entirely satisfactory. The analytical results on this fraction are not complete and analysis by the mass spectrometer showed that it is probably a mixture of several organic compounds, none of which could be identified unambiguously.

Results

(a) Photochemical Decomposition of Pure Nitrous Oxide.—If Φ_{N_2} is assumed to be 1.44[3d,e] $\Phi_{NO} = 0.82$ (if $P_{N_2O} \sim 180$ mm.). In arriving at this figure it is necessary to take account of the fact that nitric oxide and oxygen yield nitrogen dioxide at the low temperatures used for fractionation of products and that nitrogen dioxide will react with mercury (if present) to give mercuric oxide and nitric oxide. General agreement with the relative quantum yields of Zelikoff and Aschenbrand[3d,e] was found.

(b) Diethyl Ketone–Nitrous Oxide Mixtures.[11] Addition of nitrous oxide (at about 40 mm. pressure) to diethyl ketone (35 mm. pressure) affects neither the amount of carbon monoxide formed nor the amount of C_2 hydrocarbon formed at 3130 Å. at either 35 or 100°. These experiments indicate strongly that neither ethyl radicals nor propionyl radicals react with nitrous oxide at temperatures up to 100°.

(c) Nitrous Oxide–Ethane Mixtures.—The results obtained when mixtures of nitrous oxide and ethane were exposed to radiation lying in the general wave length region 1850–2000 Å. are shown in Tables I and II.

Although the intensity of the light source was not very constant it is possible to compare nitrogen produced from pure nitrous oxide with nitrogen produced in nitrous oxide–ethane mixtures in consecutive runs. The results are shown in Table III. The average of all values indicated $(N_2)_P/(N_2)_M$ to be 1.44 ± 0.05 where $(N_2)_P$ is the nitrogen from pure nitrous oxide and $(N_2)_M$ is the nitrogen under otherwise identical conditions when ethane is added. This ratio does not vary either with the C_2H_6/N_2O ratio or with total pressure and temperature.

Discussion

The mechanism proposed by Zelikoff and Aschenbrand[3d,3e] for the photochemical decomposition of pure nitrous oxide is

$$N_2O + h\nu = N_2 + O \qquad (1)^{12}$$

$$O + N_2O = N_2 + O_2 \qquad (2)$$

$$= 2NO \qquad (3)$$

$$O + O\,(+M) = O_2\,(+M) \qquad (4)$$

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[10] G. A. Castellion and A. C. Bond, to be published.

[11] The authors wish to thank Dr. J. E. Jolley for performing these experiments.

[12] An additional primary process $N_2O + h\nu = N + NO$ has also been proposed (ref. 3c). Evidence for this step is not conclusive, and it will not be considered further in this discussion.

TABLE I

PHOTOLYSIS OF NITROUS OXIDE IN THE PRESENCE OF ETHANE

(Illumination was by the 1850–2000 Å. lines of Al spark. Volume of cell = 66 cc. Φ_{N_2} assumed to be 1. Φ_{C-1} was calculated by dividing the CO_2 obtained by oxidizing the organic compounds condensable at −160° but non-condensable at −112° by the amount of N_2 formed. Φ_{C-2} was calculated by dividing the CO_2 obtained by oxidizing the organic products condensable at −112° but non-condensable at 26° by the amount of N_2 formed.)

N_2O (moles × 10^3/l.)	C_2H_6/N_2O	Illumination time (min.)	N_2 (moles × 10^6)	Φ_{CO}	Φ_{CH_4}	Φ_{H_2}	$\Phi_{C_2H_4}$	Φ_{C-1}	Φ_{C-2}	$\Phi_{\text{total carbon atoms}}$
			(A) Cell temperature = 26 ± 3°							
3.14	7.73	60	9.547	0.032	0.050	0.075	0.114	0.969	0.559	1.838
3.14	2.11	30	4.173	.034	.042	.053	.131	.534	.433	1.30
3.18	2.08	30	4.769	.038	.041	.058	.145	.528	.423	1.32
3.14	0.99	30	4.559	.037	.051	.024	.120	.242	.525	1.10
3.16	0.98	60	7.945	.052	.053	.045	.093	.232	.466	0.989
3.17	1.02	120	14.018	.060	.047	.055	.064	.190	.474	0.899
3.20	0.99	30	3.239	.033	.048	.060	...	...	...	...
6.71	1.00	45	6.733	.036	.042	.020	.118	.207	.604	1.12
6.83	.46	45	6.176	.035	.036	.024	.129	.160	.572	1.06
			(B) Cell temperature = 105 ± 2°							
3.20	1.00	45	5.169	0.050	0.069	0.093	0.169	0.225	0.768	1.48
3.20	0.99	77	8.678	.067	.066	.077	.137	.221	.702	1.33
			(C) Cell temperature = 26 ± 3°[a]							
3.48	7.27	30	4.690	0.030		0.069	0.137	0.753	0.430	1.49
3.26	7.72	30	5.511	.026		.056	.127	.961	.465	1.70
3.14	7.84	30	5.013	.024		.065	.128	.972	.453	1.70
3.09	7.85	30	5.096	.025		.063	.147	.907	.512	1.74
7.22	1.00	30	3.430	.031		.038	...	.242	.601	..
			(D) Cell temperature = 26 ± 3°[b]							
8.59	1.35	30	12.298			0.070	0.101	0.359	0.352	0.913
3.78	2.35	30	9.699			.092	.081	.604	.299	1.06
3.33	2.67	30	6.967			.074	.093	.615	.398	1.20
3.63	3.55	30	6.215			.082	.112	.696	.469	1.39
2.84	2.12	33	4.925			.075	.140	.512	.265	1.06
2.82	2.06	33	5.135			.088	.126	.483	.368	1.10
2.86	1.98	33	4.808			.110	.123	.516	.402	1.16
2.96	7.75	33	4.798			.112	.114	1.02	.533	1.78
3.26	6.25	30	5.888			.085	.117	.857	.335	1.43

[a] The quantity measured experimentally as N_2 in these runs was actually a mixture of N_2 and CH_4. The quantity listed above as N_2 is a corrected figure. The correction was made on the basis of duplicate runs where the amount of $CO + CH_4$ was determined. During the first run listed above a −112° bath was kept on the cold finger trap attached to the cell.

[b] The quantity measured as N_2 is actually a mixture of N_2 and CH_4 with the latter probably no greater than 10% of the total.

TABLE II

PHOTOLYSIS OF NITROUS OXIDE IN THE PRESENCE OF ETHANE AND ANOTHER ADDED GAS

(Illumination was by the 1850–2000 Å. lines of the Al spark. Volume of cell = 66 cc. Φ_{N_2} assumed to be 1. Φ_{C-1} was calculated by dividing the CO_2 obtained by oxidizing the organic compounds condensable at −160° but non-condensable at 112° by the amount of N_2 formed. Φ_{C-2} was calculated by dividing the CO_2 obtained by oxidizing the organic products condensable at −112° but non-condensable at 26° by the amount of N_2 formed. Cell temperature = 26 ± 3°.)

N_2O (moles × 10^3/l.)	C_2H_6/N_2O	Gas added	Gas added (moles × 10^6)	Illumination time (min.)	N_2 (moles × 10^6)	Φ_{CO}	Φ_{CH_4}	Φ_{H_2}	$\Phi_{C_2H_4}$	Φ_{C-1}	Φ_{C-2}
3.17	1.02	C_2H_4	2.33	30	4.026	0.061	0.042	0.041	...	0.296	0.573
3.23	0.98	C_2H_4	4.71	30	4.490	.046	.039	.029	...	.282	.486
3.21	.99	C_2H_4	4.75	120	12.625	.064	.034	.030	...	...	. .
3.20	1.01	O_2	1.40	30	4.163	.081	.099	.053	0.155	...	.869
3.17	1.10	O_2	1.36	30	3.440	.082	.064	.040	.230	.378	.927
3.29	1.00	O_2	1.22	60	7.476	.087	.051	.042	.096	.200	.703
3.17	.99	NO	2.83	40	3.523	.039	.088	.065	.240	.130	.706

This mechanism satisfactorily accounts for the observed products, but evidence for reactions 2 and 3 proved to be inconclusive.[13] Indeed, nitric oxide does not seem to be formed during the mercury sensitized decomposition of nitrous oxide.[4b] Since normal (^3P) oxygen atoms from nitrogen dioxide were used in the one case[13] and mercury sensitization probably produces normal oxygen atoms from nitrous oxide in the other, it has been suggested that the oxygen atoms produced by direct absorp-

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TABLE III

DETERMINATION OF THE RATIO N_2(PURE N_2O)/N_2(N_2O AND C_2H_6 MIXTURE)

(Illumination was by the 1850-2000 Å. lines of the Al spark. The amounts of N_2O were the same in a pure N_2O run and the mixture run to which it is compared. The cell volume was 112 cc. in the first set of runs reported below, in the remainder it was 66 cc. The cell temperature was 26 ± 3° in all of the sets of runs below with the exception of the last where it was 105 ± 2°. The illumination time was the same for both members of a set of runs.)

N_2O (mixture) (moles × 10^3/l.)	C_2H_6/N_2O	N_2 (pure) (moles × 10^6)	$\frac{N_2 \text{ (pure)}}{N_2 \text{ (mixture)}}$
5.75	1.39	16.246	1.45
3.63	3.55	10.143	1.63
2.84	2.12	6.923	1.40
3.26	6.25	8.306	1.41
3.26	6.25	7.915	1.34
3.26	7.92	7.593	1.38
3.14	7.80	7.265	1.45
3.14	2.11	5.839	1.40
3.20	0.99	4.857	1.50
3.20	.99	4.867	1.50
3.20	1.00	7.246	1.40

tion of radiation by nitrous oxide at wave lengths below 2000 Å. are not normal and may be either ^1S or ^1D.[3d,3e] Little is known about the mean lifetimes of ^1D and ^1S oxygen atoms or about their reactivities.

Zelikoff and Aschenbrand[3d] measured the quantum yields of various products in pure nitrous oxide at 1470 Å. and found $\Phi_{N_2} = 1.44$. At 1849 Å. the same relative quantum yields of products were found[3e] as at 1470 Å., thus affording strong evidence that the mechanisms at the two wave lengths are identical and that in all probability the primary quantum yield is unity in both cases.

If some foreign molecule is present (such as ethane) which will react quantitatively with oxygen atoms from 1, it is evident that 2, 3 and 4 will be suppressed. Φ_{N_2}(E) (the quantum yield of nitrogen formation in the presence of ethane) should then be unity. One can make runs with and without ethane and determine Φ_{N_2}/Φ_{N_2} (E). The results in Table III, column 4, give an average value for this ratio of 1.44. The agreement between the value of Φ_{N_2} and Φ_{N_2}/Φ_{N_2}(E) is extremely good and strongly supports (1) as the main if not the sole primary process.

The agreement between Φ_{N_2} and Φ_{N_2}/Φ_{N_2}(E) leads to the further conclusion that nitrous oxide is not attacked by any of the radicals or atoms in the N_2O–C_2H_6 system to give nitrogen. The failure of nitrous oxide to affect the course of the photochemical decomposition of diethyl ketone lends support to this conclusion.[11]

The nature of the attack of oxygen atoms on ethane is uncertain. Possibly more than one reaction is involved. Butane formation indicates that ethyl radicals are somehow formed in the system, but the C_2H_4/C_4H_{10} ratio is in all cases far greater than it would be if ethylene were formed solely by disproportionation.[14] Therefore either ethylene is formed by some reaction in addition to disproportionation, or butane is more rapidly destroyed than ethylene by radical or atom attack. The former conclusion is much more reasonable than the latter.

Reference to the last column in Table I will reveal that the number of carbon atoms found in products per quantum absorbed varies from 0.9 to 1.8 and in general increases with the C_2H_6/N_2O ratio. If one ethyl radical were formed per oxygen atom introduced into the system, one would expect nearly two carbon atoms to appear in products (the number might be slightly less than two if some ethane were reformed by disproportionation.) It is quite evident, therefore, that one cannot be dealing solely with the sequence of reactions

$$O + C_2H_6 = OH + C_2H_5 \qquad (4)$$

$$OH + C_2H_6 = C_2H_5 + H_2O \qquad (5)$$

or even with the single reaction

$$O + C_2H_6 = H_2O + C_2H_4 \qquad (6)$$

The products of the reaction must either (1) consume oxygen atoms very rapidly so that more than half of the oxygen atoms attack products rather than ethane or (2) prevent dissociation of nitrous oxide (possibly by absorbing radiation). The second conclusion is unlikely in view of the evidence given above about nitrogen yields in the presence and in the absence of ethane.

The rate of formation of ethylene (or more specifically $\Phi_{C_2H_4}/\Phi_{N_2}$(E)) decreases as the amount of nitrogen formed increases at a constant ratio of C_2H_6/N_2O. Thus ethylene is either destroyed so that it tends to reach a steady state, or its formation is inhibited by products. If one assumes ethylene to be destroyed by oxygen atoms, the rate constant must be about 200 times that for the attack on ethane. In Table II when the C_2H_6/C_2H_4 ratio is about 200, the change in ethylene concentration is very small. There seems to be no point in pursuing this matter further at the present time.

Previous studies of the reaction of oxygen atoms with ethane[15,16] indicate ethylene to be a product and that acetaldehyde probably is formed, along with eventually methane and carbon monoxide.

The reaction of oxygen atoms with ethylene may give the equivalent of activated ethylene oxide as suggested by Cvetanović.[17] Such molecules decompose to give hydrogen, carbon monoxide and acetaldehyde.[18] Thus most of the products of the reaction could be accounted for.

The complications arising from atom or radical attack on products (and also possibly from radiation absorption by products) make inadvisable a further discussion of reaction mechanism.

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[14] *Cf.* E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954, p. 574.

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[18] R. Gomer and W. A. Noyes, Jr., THIS JOURNAL, **72**, 101 (1950).