Photochemical Studies. LV. The Nitrous Oxide–Ethane System: Liquid Products and Competitive Rates[1]

By E. Murad and W. Albert Noyes, Jr.

The reactions of oxygen atoms produced by the direct photochemical decomposition of nitrous oxide with ethane have been studied. The relative rates of reaction of these atoms with ethane and with ethylene have been determined, the latter being about 330 times the former. Many of the products not volatile at −77° have been determined although a complete material balance has not been achieved. Many steps in the complete mechanism are suggested strongly by the natures of the products and their dependence on conditions. The oxygen atoms react so much more rapidly with some of the products than they do with ethane that the over-all mechanism is very complex.

Introduction

The nitrous oxide–ethane system has been studied with the aid of radiation absorbed solely by the nitrous oxide.[2] In nitrous oxide, at the wave lengths used, the primary process yields nitrogen molecules and oxygen atoms with a primary quantum yield of unity. The state of the oxygen atoms is almost certainly ^1D but the possibility of ^1S may not be fully excluded.

Evidence previously given[2] indicates, but does not conclusively prove, that some of the oxygen atoms from the primary process react with the ethane in a single step to give ethylene. In this respect they seem to differ markedly from normal oxygen atoms.[3,4] The reactions of oxygen atoms produced from nitrous oxide by mercury photosensitization have been studied by Cvetanovic and co-workers.[5]

The present work was undertaken to provide more conclusive evidence concerning the nature of the reaction between oxygen atoms (formed from the direct photochemical dissociation of nitrous oxide) and ethane. While there must be a reaction to give ethylene in a single step there are concurrent reactions.

Experimental

(a) The first experiments were carried out with an aluminum spark and with focal isolation to limit the wave lengths used, as previously described.[1]

The aluminum spark became too unsteady after continued use and most of the later experiments were performed with a Hanovia hydrogen lamp.[6] The radiation absorbed from the hydrogen lamp was not monochromatic but undoubtedly lay mainly in the wave length region 1900–2000 Å. It should be mentioned that in this region of the spectrum absorption by nitrous oxide is a continuum[7] so that one would

not expect a dependence of primary quantum yield on wave length.

(b) **Reagents.**—Preparations of nitrous oxide and of ethane have been described.[2]

Ethylene.—Phillips Petroleum Company research grade ethylene was distilled *in vacuo*, and the middle third collected and outgassed at −195°. Aside from the isotopic peak 29 the mass spectrograph showed no peaks higher than 28.

Acetaldehyde.—Eastman Kodak Company acetaldehyde was distilled into the line as needed. The mass spectrum showed no impurities.

Iodine.—Mallinckrodt Analytical Reagent grade iodine was sublimed into the reaction cell and outgassed.

Butane.—Cylinder butane (C.P. Matheson) was fractionated and the middle third retained. Vapor chromatography showed no impurities.

Propane.—Phillips Petroleum Company research grade propane was used without purification.

Ethyl alcohol specially purified was kindly furnished by Dr. D. H. Edison.

Methyl and Ethyl Iodides.—These reagents were obtained from Eastman Kodak Company and were fractionated by bulb to bulb distillation.

Procedure.—The quantum yields in the early part of the investigation were measured by using the photolysis of nitrous oxide as an actinometer. Each run was therefore followed by an actinometer run.

Mass spectrometry and vapor fractometry were extensively used. The mass spectrum was a Consolidated Electrodynamics mass spectrometer, model 620. Methane and nitrogen were analyzed on the mass spectrometer. The 16 and 15 peaks were used for methane and the 28 peak for nitrogen. Frequent calibrations of the sensitivity were made. A Perkin-Elmer Vapor Fractometer model 154 was used and samples were introduced through a valve. In preliminary runs the products from the Vapor Fractometer were condensed and determined on the mass spectrometer. The identity of the peaks was checked by comparing them with the cracking patterns of authentic samples. After identities of the peaks had been established, peak areas were used as measures of amounts.

When the variation of the quantum yield of nitrogen was being followed, only the fraction non-condensable at −215° (the temperature of solid nitrogen) was analyzed. This fraction consisted predominantly of nitrogen. Sometimes methane reached a maximum of 1% of the nitrogen formed. In the analysis of the liquid products the fraction non-condensable at −215° was first taken and measured. It consisted of nitrogen, methane, carbon monoxide and hydrogen. Carbon monoxide and hydrogen were oxidized over copper oxide to carbon dioxide and water, respectively. Carbon dioxide then was removed at −78° and measured, the difference was ascribed to hydrogen. The remainder of the non-condensable fraction was analyzed on the mass spectrometer.

A second fraction was collected at −168°. (The temperatures used for fractionation were produced with a LeRoy still.[8]) This fraction was analyzed on the Vapor Fractometer with a Perkin–Elmer column J. It contained most of the ethane, some nitrous oxide and 85 to 100% of the ethylene. A third fraction was collected at −158° and analyzed as the previous one. It contained the residual ethane and ethylene, some nitrous oxide and propane.

(1) This work was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF18(600)1528. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) G. A. Castellion and W. A. Noyes, Jr., This Journal, 79, 290 (1957). This paper gives references to most of the important earlier work and many of these references will not be repeated in the present article.

(3) See ref. 2 for earlier references. E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954, p. 604.

(4) L. I. Avramenko and R. V. Kolesnikova, Doklady Akad. Nauk, U.S.S.R., 89, 1037 (1953).

(5) S. Sato and R. J. Cvetanovic, Can. J. Chem., 36, 970 (1958); J. M. S. Jarvie and R. J. Cvetanovic, ibid., 37, 529 (1959).

(6) See R. P. Porter and W. A. Noyes, Jr., This Journal, 81, 2307 (1959), as well as R. P. Porter, Ph.D. Thesis, University of Rochester, 1958, for a brief discussion of the characteristics of this lamp.

(7) Cf. A. B. F. Duncan, J. Chem. Phys., 4, 638 (1936).

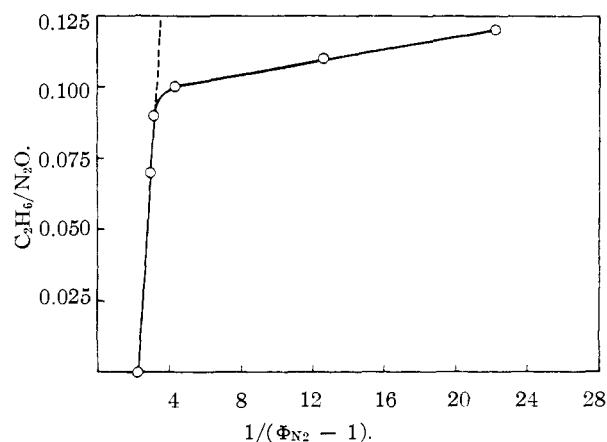(8) D. J. LeRoy, Can. J. Res., B28, 492 (1950).

Fig. 1.—Dependence of nitrogen quantum yield on ethane to nitrous oxide ratio, 25°.

A fourth fraction was collected at −149° and analyzed on a 2-meter Perkin–Elmer column A in series with a 1-meter column containing 35% Dow Corning Silicone Fluid No. 703 on acid-washed Celite, 60-100 mesh. This latter column was prepared according to the directions of Keule·manns[9] and Tenney.[10] This fraction contained nitrous oxide, butane and small amounts of acetaldehyde. A fifth fraction at −130° was analyzed on the previous column combination. It contained the residual nitrous oxide, butane and some acetaldehyde.

The remaining products were analyzed on the Vapor Fractometer by a 1-meter column containing 35% Octoil on Celite in series with a 1-meter column containing 35% polyethylene glycol 400 on Celite. The first column was prepared according to Haskins, et al.[11] and the second according to Adlard.[12] This fraction contained residual acetaldehyde, all of the ethanol and in addition there were peaks due to methanol and to propionaldehyde. At high conversions (2–3%) diethyl ether was also detected, but in the experiments reported here no diethyl ether was found. Methanol and propionaldehyde were small compared to other products and were not determined.

Water was not determined since this would have interfered with the determination of the other products. Its presence was, however, shown by Castellion.[2] There was also a small peak in the fourth fraction, which appeared as a shoulder to the peak of nitrous oxide. The presence of excess nitrous oxide made it impossible to identify this peak on the mass spectrometer.

Results

The data are given in Tables I through III and in Fig. 1. The data for Table I were obtained with the aluminum spark as a light source. Every run of ethane–nitrous oxide mixture was followed by an actinometer run. The photolysis of pure nitrous oxide was used as an actinometer, since the quantum yield of nitrogen is 1.44.[13] From the ratio of nitrogen found in the mixture to that found in the actinometer run, the quantum yield of nitrogen in the mixture was calculated. To conserve space the actinometer runs are not shown.

The data presented in Tables II and III were obtained with the hydrogen discharge lamp. Quantum yields were calculated by dividing amounts by amount of nitrogen, since it had been

(9) A. L. M. Keulemanns, "Gas Chromatography," Reinhold Publ. Corp., New York, N. Y., 1957.

(10) M. Tenney, Anal. Chem., 30, 3 (1958).

(11) J. F. Haskins, G. W. Warren, L. J. Priestly, Jr., and V. A. Yarborough, Anal. Chem., 30, 217 (1958).

(12) E. R. Adlard, in "Vapor Phase Chromatography." Edited by D. H. Desty, Butterworths Scientific Publications, London, 1957.

(13) M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys., 22, 1680, 1685 (1954).

TABLE I

TIME DEPENDENCE OF NITROGEN QUANTUM YIELD[a]

Cell volume: 66 ml.; C_2H_6/N_2O: 0.12; T: 29 ± 1°; aluminum spark; N_2O: 2.07 ± 0.18 × 10^{-4} mole

No. of deter.	Time, min.	Φ_{N_2}
1	10	1.34
3	20	1.27 ± 0.02
4	25	1.08 ± 0.03
2	30	1.05 ± 0.04

[a] To obtain the relative rates of reaction of oxygen atoms with ethylene and with ethane, respectively, the following data were obtained at 28° in the 66 ml. cell with the aluminum spark: (a) total N_2O present = 6.08 × 10^{-4} mole; (b) C_2H_6/N_2O = 0.08; (c) C_2H_4/N_2O = 2.02 × 10^{-4}; (d) N_2 formed = 3.02 × 10^{-7} moles; (e) time = 30 minutes; (f) Φ_{N_2} = 1.27. (See Discussion for calculation.)

shown[2] that the quantum yield of nitrogen in mixtures of ethane and nitrous oxide is unity when ethane was equal to or in excess of the nitrous oxide.

Discussion

Oxygen atoms formed from the direct photochemical dissociation of nitrous oxide are almost certainly not in the normal (^3P) state but are undoubtedly in a singlet state, probably ^1D[13]. In the discussion which follows, reference to oxygen atoms should be interpreted as reference to oxygen atoms formed from nitrous oxide in this way.

The following reaction scheme may be considered

$$N_2O + h\nu = N_2 + O \qquad (1)$$
$$O + N_2O = N_2 + O_2 \qquad (2)$$
$$= 2NO \qquad (3)$$
$$O + C_2H_6 = ? \qquad (4)$$
$$O + X = ? \qquad (5)$$
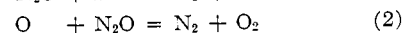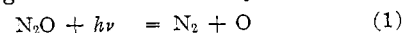
where the product of (4) and the nature of X will be discussed later. By assumption of the steady state for oxygen atoms one obtains the relationship

$$\frac{1}{\Phi_{N_2} - 1} = 1 + \frac{k_3}{k_2} + \frac{k_4(C_2H_6)}{k_2(N_2O)} + \frac{k_5}{k_2}\frac{(X)}{(N_2O)}$$

Thus a plot of $1/(\Phi_{N_2} - 1)$ vs. $(C_2H_6)/(N_2O)$ (if (X) = 0) should be linear with intercept at $(1 + k_3/k_2)$ and slope of k_4/k_2. A brief study was made in which the quantum yield of nitrogen in different mixtures was measured. The results are shown in Fig. 1. The Fig. 1 intercept has been calculated by setting Φ_{N_2} = 1.44[2,13] when $(C_2H_6)/(N_2O)$ is zero. A straight line is found for low ratios but there is a sharp bend at $(C_2H_6)/(N_2O)$ ~0.1. The slope of the lower linear portion is 9.7, i.e., k_4/k_2 = 9.7.

Deviation from linearity might be due to the formation of a product which is more reactive with oxygen atoms than ethane. A study was made of the variation of the quantum yield with time. The data are given in Table I.

It has been estimated previously[2] that oxygen atoms react with ethylene 200 times faster than with ethane. One may identify one of the products of reaction (4) as ethylene. A run was made (see Results) in which a small amount of ethylene was added and the quantum yield of nitrogen measured. Since k_4/k_2 was known from the preceding work it was possible to calculate k_5/k_2, which was found to be about 3200, i.e., k_5/k_4

TABLE II

ANALYSIS OF LIQUID PRODUCTS

Cell volume: 176 ml.; temperature: 25.7 ± 0.5°; C_2H_6/N_2O: 1.40; H_2 lamp

N_2O^a	11.14	5.76	5.87	5.32	11.14	10.57	6.01
Time (min.)	30	45	60	60	60	90	131
$R_{N_2}^b$	1.06	1.24	1.52	0.82	1.11	1.00	0.77
Φ_{CO}	0.016	0.028	0.024	.020	0.016	.012	.028
Φ_{H_2}	.076	.033	.051	.028	.053	.075	.041
Φ_{CH_4}	.020	.019	.021	.016	.012	.017	.017
$\Phi_{C_2H_4}$	.099	.096	.092	.098	.104	.080	.057
$\Phi_{C_3H_8}$	.064	.058	.076	.065	.075	.050	.035
$\Phi_{C_4H_{10}}$	.078	.042	.066	.037	.043	.058	.048
Φ_{CH_3CHO}	.031	.039	.028	.025	.046	.044	.086
$\Phi_{C_2H_5OH}$	.049	.067	.093	.078	.045	.075	.007

a Initial amount of nitrous oxide in moles × 10⁴. b Rate of nitrogen formation in moles × 10⁷ per minute.

TABLE III

PHOTOLYSIS OF NITROUS OXIDE–ETHANE IN PRESENCE OF ADDED GASES[j]

Cell volume: 176 ml.; temperature: 25 ± 0.5°; C_2H_6/N_2O: 1.40; light source: hydrogen lamp.

N_2O^a	5.63^d	5.32^h		5.87	6.28	6.01
$C_2H_6^a$	7.57	7.46	5.66	8.14	8.83	8.38
Added gas	I_2	I_2	I_2	C_2H_4	C_2H_4	C_2H_4
Amt. added gas^b	Satd.	Satd.	Satd.	12.9	11.7	9.9
Time (min.)	60	62	62	60	60	60
N_2^b	23.61	28.00		38.50	40.00	40.75
% conv.	0.42	0.52		0.66	0.64	0.68
I_L^c	381	390	390	370	378	380
Φ_{CO}	0.021	0.022		0.067	0.022	0.042
Φ_{H_2}	.069	.063		.005	.043	.047
Φ_{CH_4}	.010	.010		.014	N.d.	.016
$\Phi_{C_2H_4}$	$.038^e$	$.056^e$	4.67^b	N.d.	N.d.	N.d.
$\Phi_{C_3H_8}$				N.d.	0.090	0.099
$\Phi_{C_4H_{10}}$				0.057	.092	.083
Φ_{CH_3CHO}	$.075^f$	.055		.129	.059	.043
$\Phi_{C_2H_5OH}$		.295		.092	.089	.078
Φ_{CH_3I}	.305	.231				
$\Phi_{C_2H_5I}$	$.332^g$		10.41^b			

a In moles × 10⁴. b In moles × 10⁷. c Current through lamp in milliamperes. d Excess iodine was retained in cell at −42°. e Represents ethylene after correction for blank from third run shown. Subtraction of the blank obtained in the third run over corrected ethylene and ethyl iodide in the first and second runs. f The amount of ethyl alcohol in this run may have been zero. g Represents ethyl iodide after correcting for blank from third run. h Excess iodine was removed by mercury. In the second run it was left for 36 hours. This may possibly explain the odd result for ethyl iodide in this run. i N₂ estimated by comparison of total non-condensables in the first and fifth runs, since the nitrogen fraction was accidentally pumped out through the mass spectrometer inlet. The quantum yields for the fifth run are based on this estimate. j Blank spaces indicate zero. N.d. stands for not determined.

is about 330. This estimate of k_5/k_4 is higher than the previous one[2] but is considered to be better since it was obtained by a more direct method.

With this new information the dependence of the quantum yield of nitrogen on time may be reconsidered   It is possible to predict the general form of this dependence. Such a calculation has been carried out using the above estimate of k_5/k_2, k_4/k_2 and k_3/k_2. As will become apparent reaction 4 proceeds along more than one path, viz.

$$O + C_2H_6 \longrightarrow \text{Products not ethylene} \quad (4a)$$
$$\longrightarrow C_2H_4 + H_2O \quad (4b)$$
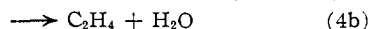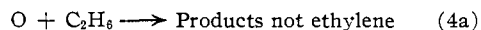
$k_{4b} = 0.2\, k_4$. (This statement will be justified later.)

The general equation if X does not reach a steady state is

$$I_a t = c - a \log \left(\frac{k_{4b}}{k_5}(C_2H_6) - (X) \right) - (X) \quad (7)$$

where c and a are constants related to the rate constants of reactions 1–5 and to the concentrations of the reactants. Equation 7 is complex and X cannot be expressed in terms of t. One may calculate t at various concentrations of X. The limiting value of the latter is $k_4(C_2H_6)/k_5$. It is next possible to relate the rate of nitrogen formation to the amount of X formed, viz.

$$d(N_2)/dt = I_a - k_2(N_2O)I_a/(f - (X)) \quad (8)$$

where f is a constant related to the individual rate constants and to the concentrations of C_2H_6 and N_2O. By plotting $d(N_2)/dt$ vs. time at various values of X, a curve is obtained, and the area under the curve up to a given time represents the total amount of nitrogen formed. Division of area by $I_a t$ gives the quantum yields at various times. Such calculations have been made with $I_a = 1.5 \times 10^{12}$ quanta/ml. sec. and $(N_2O) = 1.88$ molecules/ml. The calculated quantum yields give the right general form of curve, but an exact fit is not obtained. The calculated values of Φ_{N_2} tend to decrease at short times. This discrepancy is attributed to the fact that ethylene

can undergo reactions in addition to its reaction with oxygen atoms. Also oxygen atoms may react with other products. There is no evidence either for or against this latter possibility.

Two possibilities for (4a) need to be considered

$$O + C_2H_6 = C_2H_5 + OH \qquad (9)$$

$$O + C_2H_6 = CH_3 + CH_3O^* \qquad (10)$$

Reaction 10 could be followed by

$$CH_3O^* = CH_2O + H \qquad (11)$$

where CH_3O^* represents an electronically or vibrationally excited methoxy radical.

The results show ethylene to react rapidly with oxygen atoms. The nature of the resulting products may be stated from the discussion by Cvetanovic, et al.,[5] and must include acetaldehyde, possibly ketene, as well as methyl radicals and formaldehyde. Carbon monoxide must be formed in the present system either by radical attack on formaldehyde and on acetaldehyde, or by light absorption by these molecules. Wave lengths were present which would be absorbed readily by both of them. Hydrogen could be formed following reaction 11 or directly by decomposition of formaldehyde. Since both Φ_{CO} and Φ_{H_2} are independent of extent of conversion one might suspect rapid aldehyde disappearance as the source of both of them were it not for the fact that Φ_{CO} decreases while Φ_{H_2} increases with increasing pressure. This fact indicates strongly that carbon monoxide and hydrogen formation do not result from similar type processes. Moreover the quantum yield of acetaldehyde formation is at least approximately independent of pressure and of conversion, a further indication that acetaldehyde probably does not contribute markedly to carbon monoxide formation. Carbon monoxide formation from acetaldehyde should be accompanied by methane formation and the yield of the latter, while small, is also independent of pressure and of conversion.

The data require some method of hydrogen formation and some method of carbon monoxide formation other than the reaction of oxygen atoms with a product. Reaction 10 followed by (11) provides such a step, if formaldehyde undergoes a carbon monoxide forming reaction.

That ethylene is both formed and used up during the reaction has been shown already.[2] Ethylene does not appear, however, to reach a steady state during any of these experiments.

The formation of propane is surprising. Since neither propane nor butane is formed in the presence of iodine both undoubtedly result from radical–radical reactions. Since ethylene is formed in the presence of iodine it must not result solely from radical–radical reactions.

Ethyl alcohol is a main product but since its yield in the presence of iodine is almost if not quite zero, it is not formed appreciably by a direct reaction between oxygen atoms and ethane. It must result mainly from the reaction of hydroxyl radicals with ethyl radicals.

Reaction 11 could scarcely be written as a normal thermal reaction since its activation energy would be too great (at least 30 kcal.) to permit it to compete with the reaction

$$CH_3O + RH = CH_3OH + R \qquad (12)$$

The yield of hydrogen is relatively large and since it does not parallel that of carbon monoxide it almost certainly does not come mainly from a secondary reaction of formaldehyde. The increase of Φ_{H_2} in the presence of iodine may be due to suppression of part of the ethylene formation since ethylene is a good scavenger for hydrogen atoms.

The increase of acetaldehyde yield with added iodine must be due to an inner filter effect which decreases the photolysis of acetaldehyde.

The effect of added ethylene may be summarized as follows: (1) Φ_{H_2} decreases; (2) Φ_{CO} increases; (3) Φ_{CH_3CHO} increases; (4) $\Phi_{C_2H_5OH}$ does not change.

The first three effects can be understood easily in terms of the suggested steps and the fourth can be understood since ethyl radicals react very slowly with ethylene. Hydrogen atoms must be scavenged to some extent by the ethylene, thus forming ethyl radicals. Hence the apparent constancy of ethanol yields may result from compensating trends.

Following Cvetanovic and his co-workers[5] one may write

$$O + C_2H_4 \longrightarrow C_2H_4O^* \longrightarrow CH_3CHO \qquad (13)$$
$$\longrightarrow C_2H_3O + H$$

Ethylene oxide could not be identified among the products but this is not surprising because with ^1D oxygen atoms $C_2H_4O^*$ would have a large amount of energy.

There would seem to be very little value in writing down all of the radical reactions. Steps 4b, 9, 10, 11 and 12 followed by steps for which much proof exists already in the literature can account for the main products and for the main trends in the data.

A complete material balance could only be calculated if certain assumptions are made about the number of radicals produced by (9), (10) and (11). The work with scavengers (particularly iodine) cannot be used quantitatively because they absorb part of the radiation. While a material balance within about 20 per cent. was achieved actually it may have been much closer.

Rochester, New York