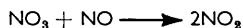


599. *The Disproportionation of Nitric Oxide: a Reaction of Nitroso-compounds.*

By M. I. CHRISTIE, C. GILLBERT, and M. A. VOISEY.

Monomeric nitrosoalkanes, formed by the thermal dissociation of dimeric nitrosomethane, or the photolysis of *t*-butyl nitrite, nitromethane, or alkyl iodides in presence of nitric oxide, cause nitric oxide to disproportionate into nitrogen dioxide and nitrogen. One molecule of nitrosoalkane can lead to the decomposition of several hundred molecules of nitric oxide by the following sequence of reactions:



The reaction of alkyl radicals with nitrogen dioxide is an important chain-breaking step.

Nitrosobenzene vapour similarly reacts with nitric oxide to form nitrogen dioxide.

In addition to methyl, another radical formed in the photolysis of acetaldehyde is efficient in disproportionating nitric oxide.

Nitroxyl (HNO) does not appear to be an effective species in the above chain of reactions.

NITRIC OXIDE is widely used to inhibit gas-phase reactions which proceed by free radical chain mechanisms. When the initiating species is an alkyl radical the initial product is a nitrosoalkane monomer, which can either dimerise or isomerise to an oxime. Dimerisation is the predominant reaction at room temperature;¹ isomerisation² is more important at higher temperatures. Another reaction attributed to monomeric nitrosoalkanes has been reported.³ An initial product of the photolysis of methyl iodide in presence of nitric oxide reacts thermally with nitric oxide to form a product whose visible absorption spectrum closely resembles that of nitrogen dioxide. The reaction is of the first order with respect to the product of the photolysis and second order with respect to nitric oxide. The extent of the reaction depends on the nitric oxide pressure. The product was thought to be either a compound $R(NO)_3$ with a high extinction coefficient or nitrogen dioxide formed in a chain reaction. An attempt to isolate nitrogen dioxide was unsuccessful.

Nitrosobenzene in solution reacts with nitric oxide to form benzene diazonium nitrate.⁴ The main products of the reaction in solution of nitrosocyclohexane with nitric oxide are nitrocyclohexane and cyclohexyl nitrate.⁵ The reaction is of zero order with respect to nitric oxide. The following chain mechanism based on the dissociation of an unstable diazonium intermediate has been suggested:⁶



¹ Gowenlock and Trotman, *J.*, 1955, 4190.

² Batt and Gowenlock, *Trans. Faraday Soc.*, 1960, **56**, 682.

³ Christie, *Proc. Roy. Soc.*, 1959, **A249**, 258.

⁴ Bamberger, *Ber.*, 1897, **30**, 506.

⁵ Donaruma and Carmody, *J. Org. Chem.*, 1957, **22**, 635.

⁶ Burrell, *J. Phys. Chem.*, 1962, **66**, 401.

Similar reaction schemes have been suggested to explain the reactions with nitric oxide of isobutene⁷ and of benzaldehyde,⁸ both of which are catalysed by nitrogen dioxide. Arden and Phillips⁹ postulate a similar mechanism involving the nitroxyl molecule (HNO) to account for the production of large yields of nitrogen and nitrogen dioxide from the pyrolysis of diethyl peroxide in presence of nitric oxide.

We have confirmed that the nitrosoalkane *monomer* is the species formed in the photolysis of alkyl iodides in presence of nitric oxide which reacts with nitric oxide. The brown product has been shown to be nitrogen dioxide. The dependence of the chain length, γ ($= \text{NO}_2/\text{R}\cdot\text{NO}$), on the concentration of monomer, nitric oxide, and nitrogen dioxide and on temperature has been studied. Other systems have been examined, including those in which the nitroxyl molecule is believed to be present, to find out whether nitroso-compounds other than alkanes react similarly with nitric oxide in the gas phase.

EXPERIMENTAL

Materials.—Methyl nitrite¹⁰ and t-butyl nitrite,¹¹ prepared from the alcohols, and methyl iodide, ethyl iodide, nitromethane, and acetaldehyde were dried (Na_2SO_4) and purified by bulb-to-bulb distillation on the vacuum line. Nitrosomethane dimer, formed¹¹ when t-butyl nitrite vapour was irradiated with light of wavelength 2537 Å from a Hanovia mercury resonance lamp, was recrystallised from ethyl alcohol. The m. p. and ultraviolet spectrum corresponded¹² with that of the *trans*-dimer. Nitrosobenzene, prepared by the oxidation of phenylhydroxylamine, was recrystallised from ethyl alcohol. Nitric oxide, from 50% sulphuric acid and saturated sodium nitrite solution in presence of mercury, was dried (P_2O_5) and distilled *in vacuo*. Nitrogen dioxide, prepared by heating lead nitrate in a stream of oxygen or by the action of oxygen on nitric oxide, was dried (P_2O_5) and distilled *in vacuo*.

Procedure.—The apparatus used for the experiments on the alkyl iodides and on acetaldehyde was similar to one described previously.¹³ The photochemical source was a Siemens 1000 w xenon arc lamp (type XB/U). The light was filtered by a cobalt sulphate–nickel sulphate solution which transmits at 2300–3400 Å. The silica reaction vessel, 15 cm. long and 3 cm. in internal diameter, was immersed in a thermostatted water tank fitted with silica end-plates. The balanced photomultiplier system could be used to measure both the iodine liberated in the photochemical reaction and the nitrogen dioxide formed in the thermal reaction. The monitoring beam of light from a tungsten filament bulb was filtered by an Ilford 604 filter, which transmits at 5000–5400 Å. The off-balance current was amplified, and recorded on a Honeywell Brown pen recorder. The system was calibrated for nitrogen dioxide by measuring the absorption in presence of varying pressure of nitric oxide over the temperature range used. The concentration of nitrosomethane was determined from the rate of production of nitrogen dioxide on the addition of a standard pressure of nitric oxide.

The experiments on the alkyl nitrites and on nitromethane were carried out at room temperature. The gases were irradiated in silica flasks of *ca.* 150 ml. capacity. For the alkyl nitrites the source of irradiation was a Hanovia mercury resonance lamp (essentially monochromatic 2537 Å light); for the nitromethane, which absorbs mainly below 2300 Å, the unfiltered light of a medium pressure mercury lamp (Hanovia, 250 w) was used. Nitrogen dioxide was determined spectrophotometrically. The reaction of aldehydes with 4-hydroxydiphenyl in sulphuric acid was used to determine formaldehyde colorimetrically.¹⁴ The irradiated vapour was condensed at -180° in a trap originally containing 1 ml. of water. The presence of nitromethane did not interfere with the method. Nitric oxide and nitrogen dioxide were distilled off before the sample was condensed in water. The nitrosomethane dimer was estimated¹² from the optical

⁷ Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480.

⁸ Kuhn and Ratiner, *Abs. Amer. Chem. Soc. 130th Meeting*, 1956, 16-0.

⁹ Arden and Phillips, *Proc. Chem. Soc.*, 1962, 354.

¹⁰ J. A. Gray and Style, *Trans. Faraday Soc.*, 1952, **48**, 1137.

¹¹ Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

¹² Gowenlock and Trotman, *J.*, 1956, 1670.

¹³ Christie, *Proc. Roy. Soc.*, 1958, *A*, **244**, 411

¹⁴ Gomer and Noyes, *J. Amer. Chem. Soc.*, 1950, **72**, 101.

density of the solution obtained by condensing the irradiated nitromethane in water. Optical densities were measured on a Unicam S.P. 500 spectrophotometer.

RESULTS

Reaction between Nitrosomethane and Nitric Oxide.—A solution of the *trans*-dimeric nitrosomethane in ether was standardised spectrophotometrically. The required volume was placed in a 135 ml. flask to which, after the ether had evaporated, 200 mm. of nitric oxide was admitted. At room temperature no reaction was observed but, at 100°C, a brown gas was formed. The reaction was complete within 1 hr. The dimer was then completely decomposed; the only solid product, identified by its infrared spectrum, was formaldoxime. The final pressure, the optical density at 4000 Å, and the pressure of gas non-condensable in liquid nitrogen were measured. The condensed products of several runs were collected. With the temperature of the trap containing the products at -78°C most of the nitric oxide was pumped away leaving a deep blue liquid. When the temperature of the trap was raised to -40° and the system had been left to regain equilibrium, the remaining nitric oxide was pumped off to leave a colourless solid. The vapour pressure of this solid and the optical densities of the saturated vapour at various temperatures were identical with those of nitrogen dioxide. The results, each the mean of two experiments in good agreement with each other, are in Table 1; $-\Delta P$ is the decrease in pressure during the reaction. p (n.c.) is the pressure of non-condensable gas.

TABLE 1.

Reaction of nitrosomethane with nitric oxide at 100°.

10 ⁶ (CH ₃ ·NO) ₂ (mole)	2·4	5·3	7·3	8·5
p (NO ₂) (mm. at 20°)	5·16	6·68	7·93	8·7
$-\Delta P$ (mm. at 20°)	3	3	4	4
p (n.c.) (mm. at 20°)	3	3	4	4
NO ₂ /2(CH ₃ ·NO) ₂	8·0	4·7	4·0	3·8

Photolysis of Alkyl Iodides.—Nitrosoalkanes were produced from the irradiation for 0·5—5 min. of mixtures containing 1—2 mm. of alkyl iodide and 10—15 mm. of nitric oxide. The concentration of nitrosoalkane was determined from the molecular iodine yield.³ Nitric oxide was added and the nitrogen dioxide formed when the thermal reaction was complete was measured. The ratio NO₂ : R·NO is denoted by γ . The results showing the variation of γ with nitric oxide pressure for nitrosomethane and for nitrosoethane at 25 and 50° are in Fig. 1. Fig. 2 illustrates the effect of the variation of nitrosomethane concentration on the yield of nitrogen dioxide at 25°. Table 2 shows the effect on γ of adding nitrogen dioxide, p (NO₂)_i, along with the nitric oxide (430 mm.), to 1·15 × 10⁻² mm. of nitrosoethane at 25°. Fig. 3 shows

TABLE 2.

Effect of NO₂ on γ .

p (NO ₂) _i (mm. at 25°)	0·00	0·07	0·32	0·68	1·22	1·85	2·70
γ	128	118	110	98	79	67	52

a plot of γ against $1/p$ (NO₂)_m where p (NO₂)_m is the mean of the initial and final pressure of nitrogen dioxide. In some of the alkyl iodide experiments the pressure of gas noncondensable at liquid nitrogen temperature was measured on a McLeod gauge. Within the experimental accuracy this pressure was equal to half the pressure of nitrogen dioxide.

Photolysis of Alkyl Nitrites.—(a) *t*-Butyl nitrite. Mixtures of *t*-butyl nitrite and nitric oxide [p (NO) = 200 mm.] were irradiated for 5 min. The results are in Table 3. The values of γ are based on a quantum yield of unity¹⁵ for the reaction (CH₃)₃C·O·NO + $h\nu$ → CH₃·NO + CH₃·CO·CH₃. The output of the mercury resonance lamp was estimated from the iodine liberated in the photolysis of a mixture of methyl iodide and nitric oxide.³

(b) *Methyl nitrite.* Methyl nitrite (1—100 mm.) in presence of 200 mm. of nitric oxide was photolysed for 1—15 min. No nitrogen dioxide was detected. Experiments using the more

¹⁵ McMillan, *J. Amer. Chem. Soc.*, 1962, **84**, 4007.

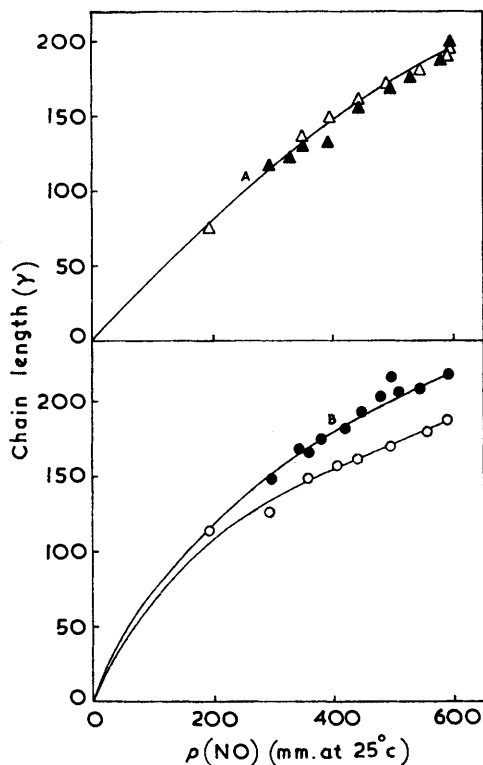


FIG. 1. Dependence of the chain length on the nitric oxide concentration.

A, Nitrosomethane: Δ 6.25×10^{-3} mm. nitrosomethane, temp. 25° ; \blacktriangle 6.5×10^{-3} mm. nitrosomethane, temp. 50° . B, Nitrosoethane: \circ 5.3×10^{-3} mm. nitrosoethane, temp. 25° ; \bullet 5.8×10^{-3} mm. nitrosoethane, temp. 50° .

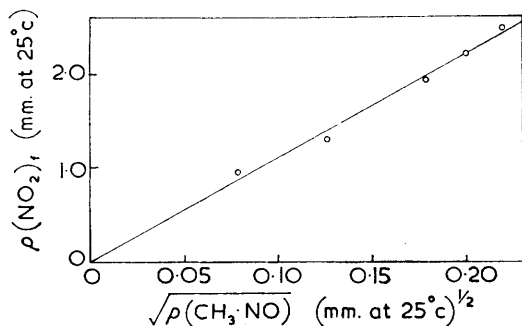


FIG. 2. Dependence of the nitrogen dioxide yield on the square-root of the nitrosomethane concentration.

$p(\text{NO}) = 415$ mm., temp. 25° .

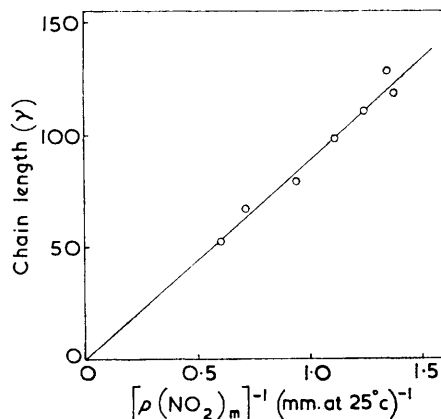


FIG. 3. Dependence of the chain length on the reciprocal of the mean concentration of nitrogen dioxide.

$p(\text{C}_2\text{H}_5\text{NO}) = 1.15 \times 10^{-3}$ mm.,
 $p(\text{NO}) = 430$ mm., temp. 25° .

TABLE 3.

Photolysis of t-butyl nitrite in presence of nitric oxide.

$p(\text{R}\cdot\text{O}\cdot\text{NO})$ (mm. at 20°)	2.0	4.0	6.0	8.0
$p(\text{NO}_2)$ (mm. at 20°)	4.33	6.61	8.02	8.94
$-\Delta P$ (mm. at 20°)	2	3	4	4
$p(\text{n.c.})$ (mm. at 20°)	2	3	4	4
γ	110	80	70	60

[1964]

The Disproportionation of Nitric Oxide.

3151

sensitive balanced photomultiplier apparatus showed that a product absorbing near 5000 Å was formed during the irradiation of a mixture of 18 mm. of methyl nitrite and 300 mm. of nitric oxide. There was no thermal reaction following the irradiation. If the product is nitrogen dioxide, the quantum yield, estimated approximately from comparison with the results for alkyl iodide photolysis, is not greater than 0.05.

Photolysis of Nitromethane.—The yields of the products formed in the photolysis of nitromethane, in the absence and in the presence of nitric oxide, are in Table 4. In each run the system was exposed to the unfiltered light of the medium pressure mercury lamp for 5 min.

TABLE 4.
Photolysis of nitromethane.

$p(\text{CH}_3\cdot\text{NO}_2)$ (mm. at 20°)	2.0	2.0	4.0	4.0	6.0	6.0	8.0	8.0
$p(\text{NO})$ (mm. at 20°)	0	198	0	196	0	194	0	192
$10^6 (\text{CH}_2\text{O})$ (mole)	0.94	0.95	1.93	1.92	2.87	2.92	3.83	3.82
$10^6 (\text{CH}_3\cdot\text{NO})_2$ (mole)	0.46	—	0.92	—	1.39	—	1.86	—
$p(\text{NO}_2)$ (mm. at 20°)	0	5.27	0	6.75	0	7.56	0	7.81

Experiments using the balanced photomultiplier system showed that the rate of disappearance of the active nitroso-compound was consistent with nitrosomethane's being the only such

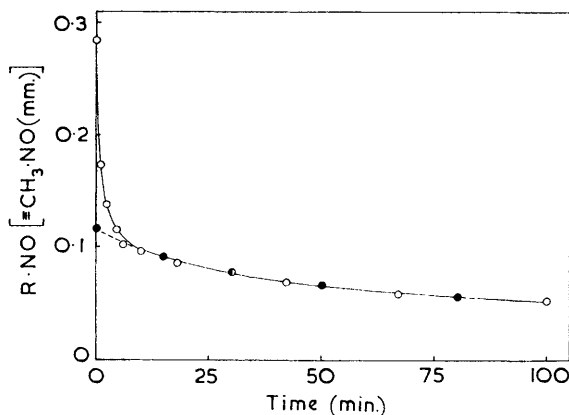


FIG. 4. Disappearance of R·NO after irradiation.

○ R·NO formed by the irradiation of a mixture of 40.5 mm. of acetaldehyde and 14 mm. of nitric oxide for 2 min. at 25°; ● CH₃·NO formed by the irradiation of 2 mm. of methyl iodide and 10 mm. of nitric oxide for 4 min. at 25°.

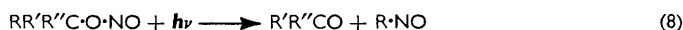
species present. More nitrosomethane was formed ($\times 2.5$) when the nitromethane was photolysed in presence of 20 mm. of nitric oxide than when it was photolysed alone.

Photolysis of Acetaldehyde.—Mixtures of acetaldehyde and nitric oxide were irradiated at 25°. Fig. 4 shows the apparent concentration of nitrosomethane monomer, as measured by the rate of production of nitrogen dioxide, at various times after irradiation. For comparison, rates of disappearance of nitrosomethane produced from the photolysis of methyl iodide in presence of nitric oxide are also plotted.

Reaction of Nitrosobenzene with Nitric Oxide.—Nitrosobenzene vapour at 25° reacts with nitric oxide to form nitrogen dioxide. The rate of production of nitrogen dioxide is proportional to the square of nitric oxide concentration; an involatile product is also formed.

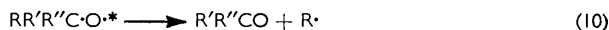
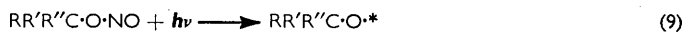
DISCUSSION

Nitrosoalkanes.—The formation of nitrosoalkanes in the photolysis of alkyl nitrites, other than methyl nitrite, indicates the following overall reaction:



The largest alkyl substituent of the α -carbon splits off to form the nitrosoalkane.¹² It is

not certain whether the nitrosoalkane is formed in a direct molecular split¹¹ or by the following mechanism involving excited alkoxy radicals:

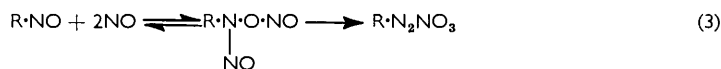


In either case the nitrosoalkane is formed in the monomeric form, which then dimerises to form either a *cis*-dimer or a *trans*-dimer.¹



At room temperature the equilibrium (2) lies well to the right when $R\cdot$ is a primary alkyl radical.¹⁶ The fact that dimeric nitrosomethane does not react rapidly with nitric oxide to form nitrogen dioxide at room temperature but does so on heating is consistent with the hypothesis that the *monomer* is the species reacting with nitric oxide. Systems in which the monomer is formed directly react readily with nitric oxide at room temperature. The yields of nitrogen dioxide show that a chain reaction is involved. The chain lengths found for the dimer (Table 1) are smaller than for the monomer (Table 3) because of some isomerisation at the higher temperature. The previous failure³ to isolate nitrogen dioxide was due to an experimental technique which was inadequate for the separation of small quantities of nitrogen dioxide in presence of a large excess of nitric oxide.

The order of the reaction in which nitrogen dioxide is produced is one with respect to nitrosoalkane and two with respect to nitric oxide,³ indicating that reaction (3) is rate-determining. This will be so if the intermediate diazonium nitrate, perhaps formed by the isomerisation of *N*-alkyl-*N*-nitrosohydroxylamine nitrite,^{2,3,6} is unstable and dissociates according to (4a). Reaction (5), of importance in the decomposition of nitrogen pentoxide,¹⁷ is rapid. The diazonium nitrate could also decompose² by elimination of nitrogen (4b).



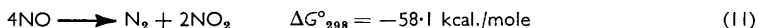
In the gas phase alkyl radicals react with nitrogen dioxide¹⁸ to form nitroalkanes (6a) or alkoxy-radicals (6b):



The most likely fate of the alkoxy-radicals in this system is to react with nitric oxide (7a) or nitrogen dioxide (7b):



For long chains the reaction is essentially the disproportionation of nitric oxide, which is energetically feasible:



A decrease in pressure consistent with this reaction was observed; the pressure of nitrogen, assumed to be the non-condensable gas, was equal to the decrease in pressure and was equal to half the pressure of nitrogen dioxide (Tables 1 and 3).

¹⁶ Christie and Frost, to be published.

¹⁷ Schott and Davidson, *J. Amer. Chem. Soc.*, 1958, **80**, 1841.

¹⁸ P. Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

[1964]

The Disproportionation of Nitric Oxide.

3153

The chain-ending steps in the above mechanism are reactions (2), (4b), (6a), and (6b). When the concentration of nitrosoalkane is low, as in most experiments reported here, the effect of the dimerisation (2) is minimised. Table 2 shows that nitrogen dioxide acts as a chain breaker. If reactions (6a) and (6b) are the only chain-ending steps, then $k_1[\text{NO}]/k_6[\text{NO}_2]_m = \gamma/2$, where $[\text{NO}_2]_m$ is the mean concentration of nitrogen dioxide and $k_6 = k_{6a} + k_{6b}$. Fig. 3 confirms this relationship between γ and nitrogen dioxide. When nitrogen dioxide is not present initially $\gamma = 2[\text{NO}_2]_m/[\text{R}\cdot\text{NO}]$ so that $k_1/k_6 = [\text{NO}_2]_m^2/[\text{R}\cdot\text{NO}][\text{NO}]$ and the yield of nitrogen dioxide, for a fixed concentration of nitric oxide, should be proportional to $[\text{R}\cdot\text{NO}]^{0.5}$ as found (Fig. 2). Estimates of k_6/k_1 can only be approximate, because if the approximation involved in taking $[\text{NO}_2]_m = 1/2([\text{NO}_2]_i + [\text{NO}_2]_f)$, and can only be upper limits since the relative importance of (4b) is not known. Alkyl nitrates have been detected¹⁶ in the products, but they could be formed by reaction (7b) only. The estimates of k_6/k_1 are in Table 5. If reaction (4b) is not important, k_6 at 25° for $\text{R}\cdot = \text{methyl}$ can be estimated, from the value¹⁹ of k_1 , to be of the order of 10^{12} ml. mole⁻¹ sec.⁻¹.

TABLE 5.
Upper limits of k_6/k_1 .

Temperature	k_6/k_1	
	25°	50°
$\text{R}\cdot = \text{Methyl}$	11, ^a 13 ^b	11 ^a
$\text{R}\cdot = \text{Ethyl}$	13, ^a 10 ^c	9 ^a

Results derived from a, Fig. 1; b, Fig. 2; c, Fig. 3.

The nitrogen, nitroalkanes, alkyl nitrates, and alkyl nitrites, which should be produced according to the above mechanism, have all been reported²⁰ to result from the interaction of alkyl radicals with nitric oxide. This reaction also accounts for the presence of nitrogen among the products²¹ of the photolysis of diethyl ketone in presence of nitric oxide.

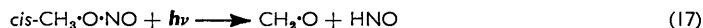
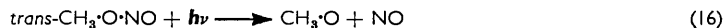
Nitroxyl.—The products of the photolysis of methyl nitrite in the gas phase include formaldehyde and nitrous oxide, which is believed to be formed from nitroxyl. Gray and Style¹⁰ suggest that nitroxyl molecules are formed from hydrogen atoms resulting from the dissociation of methoxy-radicals produced in the primary photochemical process:



Although the activation energy of reaction (13) is high²² the possibility of an excited radical decomposition as suggested¹⁵ for other alkyl nitrites cannot be excluded. Hanst and Calvert²³ suggest reaction (15) as the source of nitroxyl. Nitroxyl was detected



spectroscopically²⁴ when methyl nitrite in a solid argon matrix was photolysed at 20°K. Brown and Pimentel²⁴ suggest that the primary dissociation of *cis*-methyl nitrite differs from that of *trans*-methyl nitrite:



¹⁹ Christie, *Proc. Roy. Soc.*, 1959, A, **249**, 248; Sleppy and Calvert, *J. Amer. Chem. Soc.*, 1959, **81**, 769.

²⁰ Levy, *Ind. Eng. Chem.*, 1956, **48**, 762; McMillan, *J. Amer. Chem. Soc.*, 1961, **83**, 3018 and ref. 15; Forst and Rice, *Canad. J. Chem.*, 1963, **41**, 562; Batt and Gowenlock, ref. 2; Christie and Frost, ref. 16; Strausz and Gunning, *Canad. J. Chem.*, 1963, **41**, 1207.

²¹ Jolley, *J. Amer. Chem. Soc.*, 1957, **79**, 1537.

²² P. Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.

²³ Hanst and Calvert, *J. Phys. Chem.*, 1959, **63**, 2071.

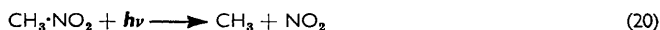
²⁴ Brown and Pimentel, *J. Chem. Phys.*, 1958, **29**, 883.

They do not exclude the possibility of nitroxyl's arising from reaction (15). At room temperature the ratio of the *trans* to the *cis* form in gaseous methyl nitrite is estimated²⁵ to be 1.86, so that both primary dissociations may be important. Although the source of nitroxyl in the photolysis of methyl nitrite is uncertain there is general agreement that it is present. If this is so it can be concluded from our results that nitroxyl is not an effective species in the chain of reactions causing the disproportionation of nitric oxide. Even if the quantum yield of nitroxyl produced is as low as 0.05, not more than one molecule of nitrogen dioxide can be produced from one nitroxyl molecule. Two factors militating against the efficiency of nitroxyl are (a) the necessity of a third body in the formation reaction (1), and (b) the possibility²⁶ of a rapid reaction between nitroxyl and hydrogen atoms:



If nitroxyl is as inefficient as appears from this investigation it is unlikely to be the only species responsible for the large yields of nitrogen and nitrogen dioxide in the pyrolysis of diethyl peroxide in presence of nitric oxide.⁹ Possibly nitrosoalkane is formed in a side reaction. Some [¹⁴N]nitrogen is formed when [¹⁵N]ammonia is photolysed²⁷ in presence of [¹⁴N]nitric oxide. The source of this nitrogen could be the reaction of nitric oxide with either nitroxyl or with a nitroso-compound formed by the amino-radical.

Photolysis of Nitromethane.—Not much quantitative information is available. The products of the photolysis of gaseous nitromethane include²⁸ nitrogen, nitric oxide, nitrogen dioxide, hydrogen, methane, carbon monoxide, carbon dioxide, formaldehyde, methyl alcohol, and possibly nitrosomethane. Nitroxyl, which has been suggested²⁹ to result from reaction (19), has been detected spectroscopically³⁰ in a mixture of nitromethane and nitric oxide subjected to flash photolysis. The absorption of light of $\lambda > 2650 \text{ \AA}$ by nitro-



methane in an argon matrix at 20°K is said²⁴ to result in the formation of *trans*-methyl nitrite. There was no evidence of a dissociation (20) to methyl radicals and nitrogen dioxide under these conditions. On the other hand Nicholson²⁸ believes that the products of the vapour-phase photolysis can be explained in terms of (20) as the primary dissociation. Reaction (20), followed by (6b) and (1), could account for the production of nitrosomethane in the photolysis of nitromethane in the absence of nitric oxide, and for the increased yield in the presence of nitric oxide. A primary dissociation (21), analogous to that suggested for nitrobenzene,³¹ is another possible source of nitrosomethane. The fact that the



formaldehyde yield is unaffected by the presence of nitric oxide may mean that it results from another primary dissociation, *e.g.*, (19). Nitromethane has a strong absorption band below 2300 Å and a weak band in the 2700 Å region. In the experiments reported here most of the light absorbed was in the wavelength region below 2300 Å. Further work on the determination of quantum yields and their wavelength dependence is necessary before any firm conclusions can be drawn about the mechanism of the photochemical decomposition.

Photolysis of Acetaldehyde.—This photolysis in presence of nitric oxide produces more than one nitroso-compound capable of causing the disproportionation of nitric oxide. One is nitrosomethane, as is to be expected from the primary dissociation to methyl radicals

²⁵ P. Gray and Pearson, *Trans. Faraday Soc.*, 1963, **59**, 347.

²⁶ Clyne and Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305.

²⁷ Srinivasan, *J. Phys. Chem.*, 1960, **64**, 679.

²⁸ Nicholson, *Nature*, 1961, **190**, 143.

²⁹ Hirshlaff and Norrish, *J.*, 1936, 1580.

³⁰ Dalby, *Canad. J. Physics*, 1958, **36**, 1336.

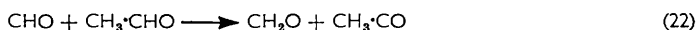
³¹ Hastings and Matsen, *J. Amer. Chem. Soc.*, 1948, **70**, 3514.

[1964]

The Disproportionation of Nitric Oxide.

3155

and formyl radicals; the other must be formed from the formyl radical or perhaps from the acetyl radical produced in the reaction ³²



There is some evidence that the formyl ³³ and the acetyl ³⁴ radicals react with nitric oxide. This new nitroso-compound disappears rapidly from the reaction mixture after irradiation has ceased. Within ten minutes the only nitroso-compound present is nitrosomethane (Fig. 4). Since this other species cannot be present in greater concentration than nitrosomethane at the end of irradiation, when only about 40% of the nitrogen dioxide produced can be attributed to nitrosomethane, it must be more efficient than nitrosomethane, *i.e.*, produce longer chains in the disproportionation reaction. If the species is $\text{CHO}\cdot\text{NO}$ a possible reaction leading to its rapid disappearance is:



The formation of nitroxyl and carbon monoxide from the reaction of formyl radical with nitric oxide has been suggested ³⁵ to occur in the pyrolysis of methyl nitrite. [*Added March 1964.*—Comparison of the formaldehyde–nitric oxide system and of the acetone–nitric oxide system with the acetaldehyde–nitric oxide system (Christie, Collins, and Voisey) indicates that the acetyl radical, but not formyl, is effective in disproportionating nitric oxide.]

Other Nitroso-compounds.—Nitrosobenzene vapour reacts with nitric oxide to form nitrogen dioxide; in solution benzenediazonium nitrate can be isolated.

The main difference between the reaction with nitric oxide of nitrosocyclohexane in solution and that of nitrosoalkane in the gas phase is that the former is of zero order ^{5,6} with respect to nitric oxide, while the latter is of second order. The zero order implies that one of the intermediates formed in the nitrosocyclohexane system is comparatively stable. It has been suggested ⁵ that the isomerisation of the substituted hydroxylamine to the diazonium nitrate is the rate-determining step.

Trifluoronitrosomethane ³⁶ reacts rapidly with nitric oxide at room temperature to form nitrogen, nitrogen dioxide, trifluoronitromethane, and a dimer, *NN*-bistrifluoromethylhydroxylamine nitrite. At -100° in organic solvents one mol. of trifluoronitrosomethane adds on two mols. of nitric oxide to form an unstable bisnitroso-derivative of trifluoromethylhydroxylamine, which decomposes at -50° .

The ability to disproportionate nitric oxide appears to be a fairly general property of *C*-nitroso-compounds. The sequence of reactions (1), (3), and (4*a*) occurs when $\text{R}\cdot$ is a primary, secondary, or tertiary alkyl,¹⁶ cyclohexyl,^{5,6} phenyl, benzoyl,⁸ or trifluoroalkyl radical,³⁶ a radical, possibly nitro-*t*-butyl,⁷ formed in the thermal decomposition of isobutene in the presence of nitrogen dioxide, and a radical, probably acetyl, formed in the photolysis of acetaldehyde. This reaction of nitroso-compounds shows that nitric oxide can initiate, as well as terminate, free radical chain reactions; the formation of nitrogen dioxide may account for the catalysis by nitric oxide of some thermal and photochemical reactions.

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³⁵ Phillips, *J.*, 1961, 3082.

³⁶ Yakubovich, Makarov, Ginsburg, Privezenteva, and Martinova, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 125 (*Chem. Abs.*, 1962, 11429^c).