BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3534—3541 (1972)

Photolysis of Nitromethane in Gas Phase at 313 nm

Koichi HONDA,* Hitoshi MIKUNI, and Makoto TAKAHASI
Department of Pure and Applied Sciences, College of Gerneal Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo

(Received June 8, 1972)

Photolysis of nitromethane in gas phase at 313.0 nm was studied at 55°C. Methyl nitrite, formaldehyde, nitrosomethane and NO were obtained as main products, their quantum yields being determined to be $\phi_{CH_3ONO}=0.22$, $\phi_{HCHO}=0.20$, $\phi_{CH_3NO}=0.06$ and $\phi_{NO}=0.10$. The dependence of the quantum yields on the pressure of quenching gases such as ethylene, *cis*-2-butene, CO_2 and NO were investigated. The quantum yields of products except formaldehyde decrease with increase in pressure of ethylene or *cis*-2-butene. The sensitized isomerization of 2-butene was also observed. The quantum yield of triplet nitromethane was determined by the Cundall method and compared with that by product analysis. Both give the identical value 0.6. Since ϕ_{HCHO} is not affected by any quencher, it is concluded that formaldehyde is formed directly from singlet excited nitromethane.

Numerous investigations have been carried out on the decomposition of nitromethane. They have revealed that the main primary process is the rupture of C–N bond as shown by (I) under various conditions, *i.e.*, continuous photolysis,[1–6] flash photolysis.[7–9] radiolysis,[4,10,11] and pyrolysis.[12]

$$CH_3NO_2 \rightarrow CH_3 + NO_2 \qquad (I)$$

In the case of pyrolysis, the main reaction subsequent to (I) is hydrogen atom abstraction by methyl radical from nitromethane, but in the case of photolysis, the recombination reaction between methyl radical and nitrogen dioxide is dominant, because hydrogen atom abstraction requires an activation energy of more than several kcal/mol. Thus, the final products in photolysis differ markedly from those in pyrolysis in spite of the same primary process. The diversity of the decomposition products of the compound suggests the complexity of secondary successive reactions.

The fact that reaction (I) is the main primary process of photolysis of nitromethane was shown by several authors. McGarvey and McGrath,[8] and Napier and Norrish[9] observed the strong absorption spectrum of methyl radical immediately after flashing nitromethane. Bielski and Timmons[6] detected the ESR spectra of methyl radical and of nitrogen dioxide during photolysis of nitromethane at 77°K. However, Christie *et al.*[3] suggested that a molecular elimination process (II), first proposed by Hirschlaff and Norrish,[1] was involved in the primary processes of photolysis of nitromethane from the fact that the yield of formaldehyde was unaffected by the addition of nitric oxide.

$$CH_3NO_2 \rightarrow CH_2O + HNO \qquad (II)$$

Moreover, Cundall *et al.*[4] suggested that in the liquid phase photolysis of nitromethane at 253.7 nm an oxygen atom elimination process (III) might be involved in the primary processes, as in the case of aromatic nitrocompounds, because so much formation of nitrosomethane cannot be explained by a cage reaction between methyl radical and nitrogen dioxide.

$$CH_3NO_2 \rightarrow CH_3NO + O \qquad (III)$$

There seems to be little doubt that the decomposition proceeds at least partly from an initial dissociation into methyl radical and nitrogen dioxide, as shown in (I), but a contribution of (II) and/or (III) also appears to be possible according to the results of the above workers.

Rebbert and Slagg[2] suggested that two excited states would be related to photo-decomposition of

---

* Present Address: The National Chemical Laboratory For Industry, 7th Division, 85 Shinshuku, Hiratsuka Kanagawa.

[1] E. Hirschlaff and R. G. W. Norrish, *J. Chem. Soc.*, **1936**, 1580.

[2] R. E. Rebbert and N. Slagg, *Bull. Soc. Chim. Belges*, **71**, 709 (1962).

[3] M. I. Christie, C. Gilbert, and M. A. Voisey, *J. Chem. Soc.*, **1964**, 3137.

[4] R. B. Cundall, A. W. Locke, and G. C. Street, "The Chemistry of Ionization and Excitation" G. R. A. Johnson and G. Scholes, Ed., Taylor * Francis Ltd., London (1967), pp. 131—140.

[5] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).

[6] B. H. J. Bielski, and R. B. Timmons, *J. Phys. Chem.*, **68**, 347 (1964).

[7] F. W. Dalby, *Can. J. Phys.*, **36**, 1336 (1958).

[8] J. J. McGarvey and W. D. McGrath, *Trans. Faraday Soc.*, **60**, 2196 (1964).

[9] I. M. Napier and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **299**, 317 (1967).

[10] S. Paszyc, *Photochem. Photobiol.*, **4**, 841 (1965)

[11] J. L. Corey and R. F. Firestone, *J. Phys. Chem.*, **74**, 1425 (1970).

[12] a) C. G. Crawforth and D. J. Waddington, *Trans. Faraday Soc.*, **65**, 1334 (1969). b) C. G. Crawforthe and D. J. Waddington, *J. Phys. Chem.*, **74**, 1425 (1970).

liquid nitromethane, in order to explain the fact that the quantum yield of methyl nitrite was larger at 253.7 nm than at 313.0 nm.

Cundall *et al.*[4] pointed out that the two excited states might be a triplet π–π* and triplet n–π* state respectively from the reduction of the quantum yield of methyl nitrite in the presence of oxygen and wavelength effect in the photolysis of liquid nitromethane. However, it is still open to question whether the decomposition process really occurs from the triplet state and if so, how much the quantum yield of the triplet state is.

We have thus attempted to obtain more information on the following problems in the photolysis of nitromethane in gas phase, when the n–π* band is irradiated.

(i) The possibility of processes other than (I).

(ii) The triplet quantum yield of nitromethane by applying the so called "Cundall method."[3]

Experimental

Materials. Commercial nitromethane (Tokyo-Kasei and Wako-Junyaku) was purified by distilling with rejection of large amounts of initial and final fractions, after dissolved nitrogen dioxide was removed by refluxing for several hours with flushing nitrogen. The pure material was stored in a 500 ml flask *in vacuo* after being dried by anhydrous sodium sulfate and distilled into high vacuum apparatus as required. All the gases were of high purity and obtained from Takachiho Kagaku. *cis*-2-Butene contained 0.44% *trans*-isomer as an impurity, but was used without further purification. Ethylene still contained 0.03% methane and 0.08% ethane after bulb-to-bulb distillation. Nitric oxide was used every time after fresh distillation to avoid contamination of nitrogen dioxide. Carbon dioxide was used without further purifications.

Apparatus and Method. The light source was an Ushio 250 D super high pressure mercury arc lamp with a Pyrex filter to eliminate light shorter than about 300 nm and with a quartz lens, diameter 5 cm and focas length 5 cm to make the incident light parallel.

Under these conditions, the light effectively absorbed by nitromethane was mainly in the 313.0 nm region. This region is the tail part of the n–π* band, and the contamination of the effect of the π–π* band adjacent to the n–π* band is considered to be eliminated. As the molar extinction coefficient of the region is very small ($\varepsilon < 4$), strong light intensity is necessary to perform experiments during the relatively short irradiation time. We did not elaborate further optical arrangements to monochromatize the incident light.

The reaction cell was a quartz cylinder with a small cold finger tip, 5 cm in diameter and 20 cm in length with a volume of 410 m*l*. The cell part was held in an electric furnace with quartz window and a stirring fan to keep constant temperature within ±1°C during the course of an experiment. It was separated from other parts by a greaseless valve.

The vacuum system was the conventional one, being set up completely mercury free to avoid the reaction of nitrogen dioxide with mercury. Sample gas was introduced into a constant volume vessel (410 m*l*). The pressure was measured by a calibrated Bourdon gauge, and the gas in the vessel was trapped into the cold finger of reaction cell with a liquid nitrogen bath. When a mixture of nitromethane with other gas was required, these procedures were repeated for each gas. The mixture prepared was kept at a reaction temperature for complete mixing at least one hour before irradiation. The usual experiments were carried out at 28 Torr (at 25°C) of nitromethane and at reaction temperature 55°C.

Actinometry. Rebbert and Slagg[2] showed that the quantum yield of ethylene formed from nitroethane is 0.074 in gaseous photolysis at 313.0 nm. Since the absorption spectrum of nitromethane was almost the same as that of nitroethane,[14] the quantum yields of products of nitromethane were easily determined. The amount of incident light in the reaction cell is determined to be 1.7×10^{17} photon/sec.

Analysis. The products were collected in a series of traps; the first was a U type tube, the second and the third were removable tubes each containing completely degassed water (about 2 m*l*) and a detachable large volume bulb (about 3 *l*). The analytical procedure was as follows.

(i) The first trap was cooled by a liquid nitrogen bath, and non-condensable gases (H_2, N_2, CO, CH_4 and most of NO) were collected in a large bulb by diffusion after the occluded gases in frozen materials were removed with freeze-melt cycles. The bulb was then detached and jointed to a Toepler pump-gas buret system. The gases were analysed by gas-chromatography (molecular sieve 5 A column, 1 m, room temp., He carrier), but the amount of NO was estimated by subtracting the moles of the other products from the total amount of noncondensable gases, because NO could not be analysed by gas-chromatography with good reproducibility. The analytical error of NO was thus larger than that of other non-condensable gases. In a very small conversion experiment, the first trap was cooled by ethyl bromide slush bath (—120°C) and gases (H_2, N_2, CO, CH_4, NO, N_2O, and C_2H_6) noncondensable at —120°C were analysed by mass-spectrometry.

(ii) The valve to the second trap cooled by a liquid nitrogen bath was opened, and the water soluble products (mainly formaldehyde and methyl nitrite) and nitromethane were dissolved in water. The aqueous solutions prepared were diluted to a constant volume and were used for quantitative analysis of formaldehyde and methyl nitrite. When both could not be measured simultaneously, they were measured separately by repeating the experiment twice.

(iii) Nitrosomethane was known to dimerize almost completely when condensed; it deposited as a white powder on the wall of the first trap together with formaldehyde polymer after procedure (ii). The materials were then vaporized by warming up to about 100°C with an electric oil bath and were condensed into the third trap cooled by a liquid nitrogen bath and dissolved into water. The analytical methods were the same as those for the second trap. The total quantity of formaldehyde was determined as the sum obtained in procedures (ii) and (iii).

The analytical methods of methyl nitrite, formaldehyde and nitrosomethane: Parker's method[15] (quantitative formation of diazo-dye by the reaction of α-naphthylamine with the nitrite ions produced by hydrolysis of methyl nitrite), Bricker's method[16] (dye formation by the reaction

---

[13] W. A. Noyes and I. Unger, "Advances in Photochemistry" **4**, p. 64, John Wiley & Sons, Inc. (1966).

[14] J. G. Calvert and J. N. Pitts, "Photochemistry" John Wiley & Sons, Inc., p. 454 (1966).

[15] C. A. Parker, *Analyst*, **74**, 112 (1949).

[16] a) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.*, **17**, 400 (1945). b) C. E. Bricker and W. A. Vail, *Anal. Chem.*, **22**, 720 (1950).

of chromotropic acid with formaldehyde in the presence of concd sulfuric acid) and UV-spectroscopy of *cis*-nitrosomethane dimer[17] (λ_{max}; 265 mn, ε_{max}; 1.0×10^4). It was confirmed that these methods were not affected by nitromethane and added gases except nitric oxide. If nitric oxide is present, Briker's method cannot be applied, but the amount of formaldehyde in the first trap is a solid polymer. The total amount of formaldehyde in the presence of nitric oxide was then estimated assuming the ratio of total amount to partial amount in the first trap is the same as the ratio in the absence of nitric oxide. Moreover, since Parker's method is also affected remarkably by dissolved nitric oxide, the analysis of methyl nitrite was carried out after the nitric oxide dissolved in the second trap solution was expelled completely by flushing with nitrogen for several hours.

The original impurity content as well as the isomerization product content of *cis*-2-butene were determined by gas chromatographic analysis (active alumina with 2% squalane column, 2 m, 100°C, N_2 carrier, FID).

Miner products not analysed were checked also by gas chromatography (DOP, 2 m, 100°C, He carrier, TCD).

Analytical methods described above were modified in some cases.

Results

(I) Quantum Yields of Products at Small Conversions. In the gas phase photolysis of nitromethane (55°C, 28 Torr at 25°C), the products of quantum yields more than 0.05 at small conversions were methyl nitrite, formaldehyde, nitric oxide, nitrosomethane and nitrous oxide, their amounts decreasing in this order. When irradiation was prolonged, CO joined the main products (up to $\phi_{CO}=0.13$ at 90 min. irradiation) and the quantum yields of main products (methyl nitrite, formaldehyde and nitric oxide) decreased with the irradiation time (up to $\phi_{CH_3ONO}=0.07$, $\phi_{CH_2O}=0.10$ at 90 min. irradiation).

Minor products analysed quantitatively were methane, hydrogen, carbon monoxide and nitrogen. Other minor products detected in gas-chromatograph were ethane, methanol, water, methyl nitrate and carbon dioxide. Nitrogen dioxide was not detected in the final products (at least at small conversions) by mass spectroscopic analysis. This agreed with the results of earlier workers,[2,4] although the possibility of loss during the course of pumping gaseous products with a Toepler-pump was not completely excluded, since nitrogen dioxide is very reactive with mercury.

As shown in Fig. 1, formaldehyde is the main product even at such a small conversion as 0.3% (at 1 min irradiation), differing from the result of Rebbert and Slagg.[2] Process (III), if it exists at all, would not be so important at least under the experimental condition, since the quantum yield of nitrosomethane is so small.

The quantum yields of products larger than 0.05 are summarized in Table 1.

The quantum yields of minor products determined by mass spectroscopy at small conversions (1 min. and 2 min. irradiations) were $\phi_{H_2}=0.02$; $\phi_{CH_4}=0.02$; $\phi_{N_2+CO}=0.05$, and except CO, they decreased to one tenth, when irradiated longer than 15 min.

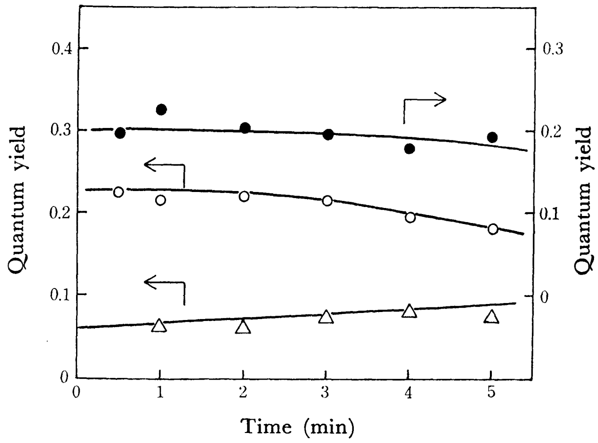


Fig. 1. The quantum yields of methyl nitrite, formaldehyde and nitrosomethane against irradiation time within 5 min. ○; methyl nitrite, ●; formaldehyde, △; nitrosomethane

TABLE 1. SUMMARY OF THE QUANTUM YIELDS OF MAJOR PRODUCTS

($\phi>0.05$)

Product	Quantum yield
CH_3ONO	0.22[a]
CH_2O	0.20[a]
CH_3NO	0.06[a]
NO	0.10[b]
N_2O	0.05[b]

a) Obtained by extrapolating the irradiation time to zero in Fig. 1.

b) Obtained from mass spectral results from 1 and 2 min. irradiation products.

(II) Effects of Added Gases. The variations of quantum yield of methyl nitrite, formaldehyde and nitric oxide with the pressures of added gases, *i.e.*, ethylene, *cis*-2-butene, NO or CO_2 are shown in Fig. 2a, 2b, 2c and 2d.

The quantum yield of formaldehyde is almost independent of the added gases, ethylene or *cis*-2-butene, while those of methyl nitrite and nitric oxide decrease with increase in the pressure of olefins (Fig. 2a and 2b). In other words, the formation of methyl nitrite and nitric oxide are suppressed by the presence of olefins, but that of formaldehyde is little affected. In the case of addition of *cis*-2-butene, isomerization of *cis*-2-butene to *trans*-isomer occurred simultaneously.

Minor products also decreased with increasing pressures of olefins, and at pressures above several tens of Torr, methane and hydrogen were below detectable limit. To know whether the decrease of the quantum yield of methyl nitrite might be due to the scavenging action of methyl radicals by the olefins, the amount of methyl radicals produced in the excess of ethylene was estimated from the yield of hydrocarbons (CH_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}). It was found that the quantum yield of methyl radical is at most 0.01, if excess ethylene exists.

---

[17] a) H. T. J. Chilton, B. G. Gowenlock, and J. Trotman, *Chem. and Ind.* (london), **1955**, 538. b) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, **1956** 1670.

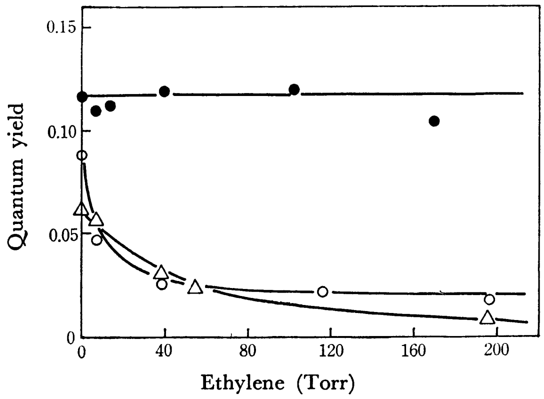


Fig. 2a. The quantum yields of methyl nitrite, formaldehyde and nitric oxide against the press. of ethylene. Irradiation time; 60 min.
○; methyl nitrite, ●; formaldehyde, △; nitric oxide

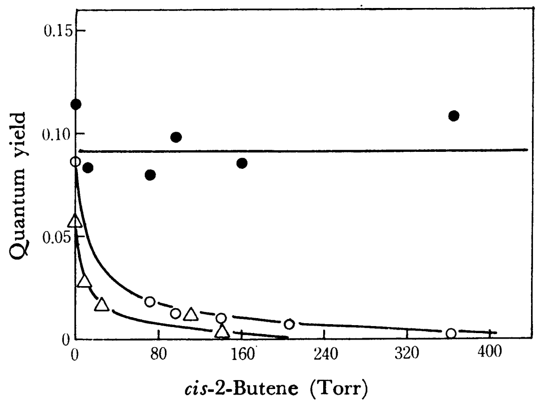


Fig. 2b. The quantum yields of methyl nitrite, formaldehyde and nitric oxide against the press. of *cis*-2-butene. Irradiation time; 60 min.
○; methyl nitrite, ●; formaldehyde, △; nitric oxide

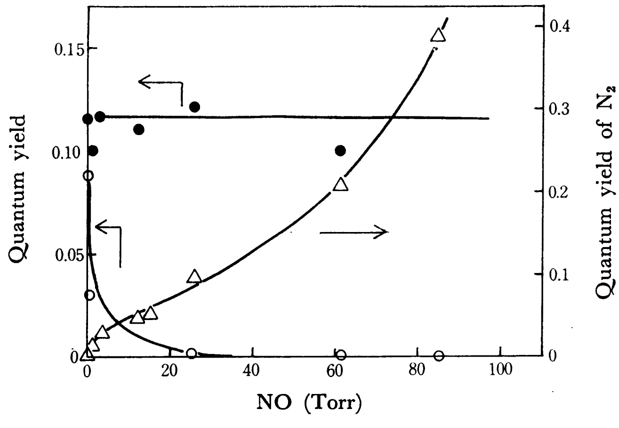


Fig. 2c. The quantum yields of methyl nitrite, formaldehyde and nitrogen against the press. of nitric oxide. Irradiation time; 60 min.
○; methyl nitrite, ●; formaldehyde, △; nitrogen

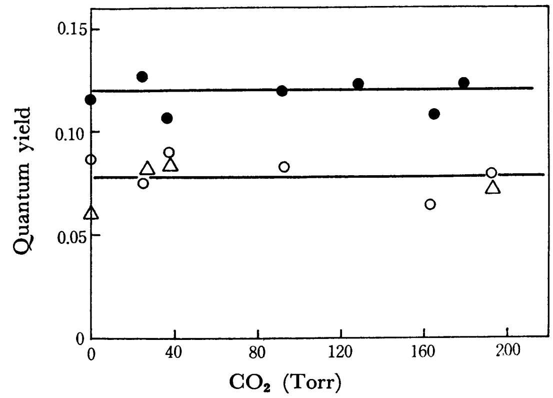


Fig. 2d. The quantum yields of methyl nitrite, formaldehyde and nitric oxide against the press. of CO_2. Irradiation time; 60 min.
○; methyl nitrite, ●; formaldehyde, △; nitric oxide

The quantum yield of methyl nitrite decreased sharply in the presence of nitric oxide and became almost zero above 25 Torr of nitric oxide (Fig. 2c). In this case, methane was not detectable at all and on the contrary, nitrogen increased remarkably with nitric oxide pressure.

As established by many workers, nitrogen formation from nitric oxide is caused by disproportionation ($4NO \rightarrow N_2 + 2NO_2$) under the catalytic action of methyl radical. The sharp increase of nitrogen and the failure of methane formation therefore supports the view that process (I) to form methyl radical is involved in the primary processes of nitromethane photo-decomposition.

That the yield of formaldehyde was not affected by the addition of nitric oxide suggests that almost all the formaldehyde should be formed by the molecular elimination process like (II).[3]

The effect of added CO_2 was not noticeable either in the main products formation as shown in Fig. 2d or in minor products formation. Hence, the vibrationally excited states quenchable by added CO_2 is not supposed to be involved in the photo-decomposition of nitromethane.

(III) Effect of Reaction Temperature. In order to know the temperature effect of the primary processes of nitromethane photolysis, the quantum yields of methyl nitrite and formaldehyde were measured in the temperature range 25—200°C. The results shown in Fig. 3 indicate that methyl nitrite formation was

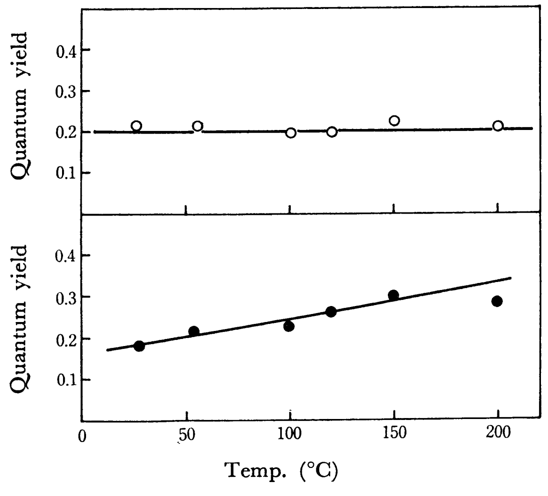


Fig. 3. Temperature dependence of the quantum yields of methyl nitrite, and formaldehyde. Irradiation time 1 min.
○; methyl nitrite, ●; formaldehyde

nearly temperature independent, whereas formaldehyde formation increased with increasing temperature. The increase of formaldehyde with reaction temperature cannot be ascribed to the pyrolytic formation of formaldehyde by the degradation of $\cdot CH_2NO_2$ radicals. If this is the case, the consumption of methyl radical by the abstraction reaction with nitromethane would be expected with increase of reaction temperature, resulting in a decrease of methyl nitrite with temperature. The activation energy of formaldehyde formation was estimated to be 0.7 kcal/mol.

Discussion

(I) Reaction Mechanism. The effect of added gases in the photolysis of nitromethane was shown to be as follows.

(i) Addition of *cis*-2-butene caused a decrease of the quantum yield of methyl nitrite and nitric oxide. A part of *cis*-2-butene was simultaneously isomerized to *trans* form, whereas it little affected formaldehyde formation. This implies that the processes to yield methyl nitrite and nitric oxide proceed through a triplet state of nitromethane, but not those for formaldehyde formation, since the isomerization of *cis*-2-butene is thought to take place through triplet 2-butene formed by the photosensitization of a triplet nitromethane.

(ii) Ethylene acts in the same way as *cis*-2-butene, although less effectively, suggesting that ethylene also can quench the triplet state of nitromethane. Thus the lowest triplet energy of nitromethane is supposed to be greater than that of ethylene (about 78 kcal/mol).

(iii) The rate of methyl nitrite and methane formation decreased to zero while nitrogen formation increased remarkably on addition of nitric oxide, showing that the main primary process is the C–N bond fission (I), and methyl radical formed is scavenged by nitric oxide to give nitrosomethane, which reacts further with nitric oxide to produce nitrogen.

Since nitric oxide does not affect the rate of formaldehyde formation, formaldehyde is not formed by a radical reaction but by a molecular elimination reaction like process (II).

The above results suggest that process (I) takes place from the lowest triplet state of nitromethane, $T_{n-\pi^*}$, and process (II) takes place from such a very short lived state as not quenched by added gases, probably the lowest excited singlet state $S_{n-\pi^*}$.

The proposed reaction mechanism is as follows, where elementary reactions supposed to be important at a small conversion are underlined. Rate constants determined recently by several authors are shown in Table 2.

TABLE 2. SUMMARY OF RATE CONSTANTS USED IN OUR CALCULATIONS[a)]

Rate const	l/mol, sec
k_{9a}	4.1×10^{9} [18,19,b)]
k_{9b}	7.9×10^{9} [18,19,b)]
k_{9c}	$\ll k_{9a}, k_{9b}$ [19,c)]
k_{10a}	1.8×10^{8} [20)]
k_{10b}	2.4×10^{9} [18)]
k_{10c}	1.0×10^{8} [18,19)]
k_{10d}	2.3×10^{7} [20)]
k_{10e}	3.0×10^{10} [20)]
k_{10f}	1.2×10^{10} [c)20,d)]
k_{10g}	4.8—14.4×10^{6} [20)]

a) Rate const of (9a), (9b) and (10c) are based on the data at 90°C, and the others at 25°C. However, they can be all applied to the present case at 55°C, since activation energies of the reactions are nearly zero.
b) Calculated values from the ratio of k_{9a}, k_{9b} and k_{10c} to k_{10b} determined by Phillips and Shaw, and the value of k_{10b} obtained by Basco *et al.*
c) Reaction (9c) is not important in gaseous reactions, since CH_3O-NO bond undergoes rupture easily.
d) A tentative value determined by McGraw *et al.*

$$N \xrightarrow{h\nu} N_S$$

($\underline{1}$) $N_S(+M) \rightarrow N \quad + (M)$

(2) $N_S \rightarrow N \quad + h\nu_f$ (actually not observed)

($\underline{3}$) $N_S \rightarrow N_T$

($\underline{4}$) $N_S \rightarrow CH_2O + HNO$

($\underline{5}$) $N_T \rightarrow CH_3\cdot + NO_2$

(6) $N_T(+M) \rightarrow N \quad (+M)$

(7) $N_T \rightarrow N \quad + h\nu_p$ (actually not observed)

($\underline{8}$) $N_T + Q \rightarrow N \quad + Q_T$

($\underline{9a}$) $CH_3\cdot + NO_2 \rightarrow CH_3NO_2$

($\underline{9b}$) $CH_3\cdot + NO_2 \rightarrow CH_3O\cdot + NO$

($\underline{9c}$) $CH_3\cdot + NO_2 \rightarrow CH_3ONO$

($\underline{10a}$) $CH_3O\cdot + NO \rightarrow CH_3ONO$

($\underline{10b}$) $CH_3\cdot + NO \rightarrow CH_3NO$

(10c) $CH_3O\cdot + NO_2 \rightarrow CH_3ONO_2$

(10d) $CH_3O\cdot + NO \rightarrow CH_2O + HNO$

($\underline{10e}$) $CH_3O\cdot + HNO \rightarrow CH_3OH + NO$

(10f) $CH_3O\cdot + CH_3O\cdot \rightarrow CH_3OH + CH_2O$

($\underline{10g}$) $HNO + HNO \rightarrow H_2O + N_2O$

(10h) $CH_3\cdot + CH_3O\cdot \rightarrow CH_4 + CH_2O$

where N_S denotes the lowest excited singlet stage, N_T the lowest triplet state, N the ground state nitromethane and Q the triplet quenchers, respectively.

On the basis of the proposed reaction scheme, we can estimate the quantum yield of reaction (5), ϕ_5, to be 0.6 from the sum of quantum yields of the products at small conversions (Table 1) with the help of rate constants (k_{9a} and k_{9b}) reported by Philips and Show,[19] *viz.*, the quantum yield of reaction (9b), ϕ_{9b}, sum of ϕ_{CH_3ONO}, ϕ_{CH_3NO} and ϕ_{NO} is no less than 0.4, because these products are formed only from the sub-

---

18) N. Basco, D. J. L. James, and R. D. Suart, *Int. J. Chem. Kinet.*, II, 215 (1970).

19) L. Phillips and R. Shaw, Symp. Combust, 10th, Univ. Cambridge, England, 1964, pp. 453—461 (1965).

20) G. E. McGraw and H. S. Johnston, *Int. J. Chem. Kinet.*, I, 89 (1969).

sequent reactions of (9b), keeping in mind that reaction (9c) is negligible; the quantum yield of reaction (9a), ϕ_{9a}, is estimated to be about 0.2 on the basis of the ratio of the rate constants obtained by Phillips and Shaw;[19] Thus, ϕ_5 is estimated to be about 0.6.

The primary quantum yield of reaction (4), ϕ_4, the observed quantum yield of formaldehyde at small conversions, is about 0.2. The contribution of (10d), (10f) and (10h) is considered to be small for the production of formaldehyde.

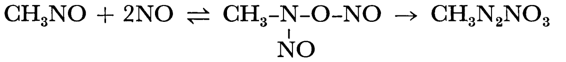
The mechanism of CO formation might be complex; CO seems to be formed by the secondary photolysis of methyl nitrite and formaldehyde and/or by oxidation reaction of oxygen atom formed by the photolysis of nitrogen dioxide since CO formation is appreciable only on being irradiated for a long time.

Hydrogen may be formed also by the secondary photolysis of formaldehyde. Formation of small amounts of methanol, water, nitrous oxide and methyl nitrate is explained by the reactions (10e), (10f), (10g) and (10c).

In the case of nitric oxide addition, reaction (5) is followed by the chain reactions described below as established by several researchers.[3,9,21,22)]

(10b) $CH_3\cdot + NO \rightarrow CH_3NO$

(11)



$CH_3NO + 2NO \rightleftharpoons CH_3\text{-}\underset{NO}{\underset{|}{N}}\text{-}O\text{-}NO \rightarrow CH_3N_2NO_3$

(12a) $CH_3N_2NO_3 \rightarrow CH_3\cdot + NO_3 + N_2$

(12b) $CH_3N_2NO_3 \rightarrow CH_3NO_3 + N_2$

(13) $NO_3 + NO \rightarrow 2NO_2$

(14) $CH_3NO \rightarrow CH_2\text{=}NOH$

(15) $2CH_3NO \rightarrow (CH_3NO)_2$

(16) $CH_3NO + NO_2 \rightarrow CH_3NO_2 + NO$

Although reaction (9a) and reactions subsequent to (9b) might act as chain termination reactions to some extent, (14), (15) and (16) may become dominant as pressure of nitric oxide is increased, since we cannot detect methyl nitrite if nitric oxide is present in more than several Torr.

Formation of a trace of nitrogen without addition of nitric oxide may be interpreted also in terms of the above reactions. Since it was confirmed that HNO radical and methoxy radical have no ability to act as a chain carrier in the above disproportionation reactions of nitric oxide,[3] the anomalous increase of nitrogen in the presence of nitric oxide should be caused by (10b) and the successive reactions.

We confirmed that the plot of the quantum yield of nitrogen against the second power of nitric oxide pressure satisfied the linear relationship above several Torr of the pressure (not shown in the figure). This suggests that (12) is the rate determining step of these nitrogen formation reactions.

(II) Sensitized Isomerization of cis-2-*Butene by Nitromethane and Photostationary State.* It is generally accepted that the quantum yield of triplet state can be determined by the "Cundall method."[13] However, in order to apply this method, it should be confirmed that the isomerization does not occur through radical mechanism (Schenck mechanismm).[23]

Main radicals formed by the decomposition of nitromethane are methyl, methoxy, nitrogen dioxide, nitric oxide and HNO radical. Cundall and Davies[24,25] confirmed in their study of the photolysis of acetone and acetaldehyde that methyl radical does not cause the isomerization of 2-butenes. It is known that nitrogen dioxide and nitric oxide act as a catalyst of the thermal isomerization of 2-butenes and they reduce the activation energy from 63 kcal/mol to 12 kcal/mol[26] and 26 kcal/mol[27] respectively. However, under our experimental conditions (50°C), isomerization by either species must be negligible, because the calculated rate of isomerization is at least ten times slower than our experimental result. HNO radical may react with *cis*-2-butene in the same way as formyl radical to form secondary butyl radical and nitric oxide, but the secondary butyl radical is expected to decompose into methyl radical and propylene but not to reproduce 2-butenes. Although there seems to be no data on reactions of methoxy radical with olefins, our experimental results where the quantum yield of *trans*-2-butene increased with increasing *cis*-2-butene pressure in spite of the decrease of the quantum yield of methyl nitrite suggest that isomerization by methoxy radicals is less probable.

Another possibility may be isomerization through butenyl radical which may be formed by the abstraction of hydrogen atom from 2-butene by some radical. However, this is also less likely under our experimental conditions, since it requires activation energy of more than several kcal.

If the possibilities of isomerization through radical mechanism can be neglected, sensitized-isomerization by triplet nitromethane should be considered. For photosensitized isomerization to be possible, triplet energy of sensitizer should be larger or at least not much less than that of 2-butene. So far neither phosphorescence[28] nor S–T absorption spectrum has been observed, and we cannot predict from spectroscopic data whether the sensitized isomerization of 2-butene by nitromethane is possible or not. However, when we see that sensitized isomerization actually takes place, we can presume that the triplet level of nitromethane lies above that of 2-butene (76 kcal)[29] or ethylene (78 kcal).[29]

We shall discuss the sensitized isomerization of 2-

---

[21] a) W. Frost and O. K. Rice, *Can. J. Chem.*, **41**, 562 (1963). b) O. P. Strauss and H. G. Gunning, *ibid.*, **41**, 1207 (1963).

[22] J. R. Gilbert, R. M. Lambert and J. W. Linnett, *Trans. Faraday Soc.*, **66**, 2837 (1970).

[23] N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

[24] R. B. Cundall and A. S. Davies, *Proc. Roy. Soc. Ser. A*, **290**, 563 (1966).

[25] R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 2793 (1966).

[26] J. L. Sprung, H. Akimoto, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **93**, 4358 (1971).

[27] R. B. Cundall, "Progress in Reaction Kinetics" Pergamon Press (1964). Vol. 2, 182.

[28] Dr. Kuboyama, The National Chemical Laboratory For Industry, kindly attmepted to measure the phosphorescence of nitromethane, but it could not be observed at least in the sensitivity range of the instrument,

butene by nitromethane more in detail. Completely in the same way as Cundall et al.[30] and Lee *et al.*,[31] the following reaction scheme is assumed for sensitized isomerization.

$$
\begin{array}{lllll}
\text{(8a)} & N_T + B_{cis} & \rightarrow & N + B_{T\,cis} \\
\text{(8b)} & N_T + B_{trans} & \rightarrow & N + B_{T\,trans} \\
\text{(17a)} & B_{T\,cis} & \rightarrow & B_{T\,trans} \\
\text{(17b)} & B_{T\,trans} & \rightarrow & B_{T\,cis} \\
\text{(18a)} & B_{T\,trans} & \rightarrow & B_{trans} \\
\text{(18b)} & B_{T\,cis} & \rightarrow & B_{cis}
\end{array}
$$

where N_T denote triplet nitromethane, B_{cis} and B_{trans} *cis* and *trans*-2-butene, $B_{T\,cis}$ and $B_{T\,trans}$ triplet of 2-butene in *cis* and *trans* form respectively. The following rate expressions are derived in the usual way, under steady state conditions. The initial rate of isomerization of *cis*-2-butene to *trans* form, $R_{c\to t}$, under a fixed pressure of nitromethane and light intensity and in the absence of *trans*-2-butene, is given below.

$$
\begin{aligned}
R_{c\to t} = & \left(\frac{I_a}{k_1+k_2[\mathrm{M}]+k_3+k_4}\right) \\
& \times \left(\frac{k_{17a}k_{18a}}{k_{17a}k_{18a}+k_{17b}k_{18b}+k_{18a}k_{18b}}\right) \\
& \times \left(\frac{k_{8a}[\mathrm{B}_{cis}]}{k_5+k_6[\mathrm{N}]+k_7+k_{8a}[\mathrm{B}_{cis}]}\right)
\end{aligned} \tag{1}
$$

An analogous equation can be derived for reversed isomerization, and the ratio $R_{c\to t}/R_{t\to c}$ is expressed simply as follows.

$$R_{c\to t}/R_{t\to c} = k_{17a}k_{18a}/k_{17b}k_{18b} \tag{2}$$

In addition, in the photostationary state (abbreviated as pss), the ratio $([\mathrm{B}_{trans}]/[\mathrm{B}_{cis}])_{\mathrm{pss}}$ can be expressed as follows.

$$([\mathrm{B}_{trans}]/[\mathrm{B}_{cis}])_{\mathrm{pss}} = \frac{k_{8a}k_{17a}k_{18a}}{k_{8b}k_{17b}k_{18b}} = \frac{k_{8a}R_{c\to t}}{k_{8b}R_{t\to c}} \tag{3}$$

In the benzene-sensitized isomerization of 2-butene, Cundall *et al.*[30] reported the value of 1.37 for $R_{c\to t}/R_{t\to c}$, but later Lee et al.[31] obtained the value of 1.02. At the same time, for the value of $([\mathrm{B}_{trans}]/[\mathrm{B}_{cis}])_{\mathrm{pss}}$, Cundall and his co-workers gave the value of 1.37, assuming that k_{8a}/k_{8b} is unity (no difference between *cis*- and *trans*-2-butene) on the basis of their observation that several efficient quenchers have identical quenching cross sections for triplet benzene but this observation seems to be supported neither by Tanaka *et al.*[32] nor Lee's group. In order to determine the exact value of $([\mathrm{B}_{trans}]/[\mathrm{B}_{cis}])_{\mathrm{pss}}$, it is preferable to carry out the isomerization experiment starting from a mixture of *cis*- and *trans*-2-butene whose initial composition is already near the stationary state. Lee *et al.*[31] obtained the value of 0.92 by this method. Applying this technique to nitromethane-sensitized isomerization, we obtained the value of 0.90, irradiating a sample containing 28 Torr of nitromethane and 8.7 Torr of a mixture of *cis*- and *trans*-2-butene in an equal amount (Table 3). For the sake of comparison, the pss ratios for several sensitizers are given in Table 5. It is interesting that the organic sensitizers investigated so far give the value of around 0.9 for the pss ratio except Cundall's value for benzene. Larger quenching cross section of *trans*-2-butene to these organic sensitizers may be interpreted either in terms of the small difference in triplet energy of *cis*- and *trans*-2-butene or the difference in the ease of collision complex formation between the sensitizer and the quencher, but no well-established explanation has been given yet.

TABLE 3. VARIATION OF *trans*/*cis* WITH IRRADIATION TIME[a)]

Time (hr)	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
trans*/*cis	1.01	0.99	0.98	0.96	0.94	0.92	0.90	0.90	0.90

a) Nitromethane press.; 28 Torr, *trans*-, *cis*- mixture press.; 8.7 Torr, photolysis temp.: 55°C.

(III) Quantum Yield of Triplet Nitromethane by the Cundall Method and by Product Analysis. We determined the quantum yield of triplet nitromethane according to the ordinary procedure of the Cundall method. A good linear relationship is obtained between $1/\phi_{\mathrm{B}c\to t}$ and $1/[\mathrm{B}_{cis}]$ (Fig. 4) where $\phi_{\mathrm{B}c\to t}$ is the quantum yield of *trans*-2-butene from *cis*-form in the absence of *trans* form, *viz.*, $\phi_{\mathrm{B}c\to t}=R_{c\to t}/I_a$.

The linear relationship is consistent with the following equation which is derived from equation (1).

$$
\begin{aligned}
1/R_{c\to t} = & \frac{k_1+k_2[\mathrm{M}]+k_3+k_4}{k_3 I_a} \\
& \times \left(\frac{k_{17a}k_{18a}+k_{17b}k_{18b}+k_{18a}k_{18b}}{k_{17a}k_{18a}}\right) \\
& \times \left(\frac{k_5+k_6[\mathrm{N}]+k_7}{k_{8a}[\mathrm{B}_{cis}]}+1\right)
\end{aligned} \tag{4}
$$

As shown in Fig. 4, the reciprocal of intercept gives the value of 0.3 which corresponds to $\phi_{c\to t}$ at an infinitely high pressure of *cis*-butene. Although we did not measure the ratio $R_{c\to t}/R_{t\to c}$ for nitromethane, we may assume that it is approximately unity as Haninger determined for benzene-sensitization, if we assume that

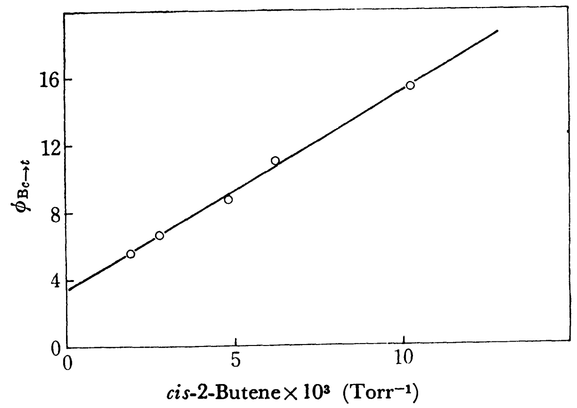


Fig. 4. Reciprocal-reciprocal plot of the quantum yields of triplet 2-butene and the press. of *cis*-2-butene.

---

[29] M. W. Schmidt and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 3579 (1970).

[30] R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

[31] E. K. C. Lee, H. O. Denschlar, and G. A. Haninger, *J. Chem. Phys.*, **48**, 4547 (1968).

[32] M. Tanaka, T. Terao, and S. Sato, This Bulletin, **38**, 1645 (1965).

the ratio is independent of the triplet energy of sensitizer. In addition, we may assume that k_{17a} and k_{17b} are much larger than k_{18a} and k_{18b}, although Haninger pointed out there is some doubt as to this assumption. Thus, we obtain the following relationship.

$$\begin{aligned}\phi_3 = \phi_{\mathrm{N_T}} = \phi^{\infty}_{\mathrm{B_T}} &= (\phi^{\infty}_{\mathrm{B}_{c\to t}} + \phi^{\infty}_{\mathrm{B}_{t\to c}}) \\ &= \phi_{\mathrm{B}c\to t}(R_{c\to t}+R_{t\to c})/R_{c\to t} \\ &\doteqdot 2R_{c\to t}/I_a = 2\phi_{\mathrm{B}c\to t} = 0.6 \qquad (5)\end{aligned}$$

Using the obtained values ϕ_3 and ϕ_4, we can estimate the value of ϕ_1 to be 0.2 as the difference $(1-\phi_3-\phi_4)$, neglecting the fluorescence process.

We showed that the quantum yield ϕ_5 is 0.6 which is calculated from the product analysis. Therefore, ϕ_{NT} obtained by the Cundall method is consistent with ϕ_5 obtained by product analysis, indicating that the non-radiative process (6) and radiative process (7) are not important, even though they exist. The quantum yields of reactions (1)—(7) are summarized in Table 4. Equation (4) can be made simpler as follows.

TABLE 4. SUMMARY OF THE QUANTUM YIELDS OF REACTIONS (1)—(5)

ϕ_1	0.2
$(\phi_2$	0)
$\phi_3(\phi_T)$	0.6
ϕ_4	0.2
ϕ_5	0.6
$(\phi_6$	0)
$(\phi_7$	0)

$$1/\phi_{\mathrm{BT}} = \left(\frac{k_1+k_3+k_4}{k_3}\right)\left(\frac{k_5}{k_{8a}[\mathrm{B}_{cis}]}+1\right) \qquad (6)$$

From the ratio of slope to intercept in Fig. 4, the ratio of rate constant for the dissociation to that for energy transfer, k_5/k_{8a}, is calculated to be 1.7×10^{-2} mol/l at 55°C. Since nitro compounds resemble carbonyl compounds in the behaviors of their absorption and phosphorescence spectra of n-π^* transition and 2-butene isomerization, it may be interesting to compare triplet quantum yield ϕ_T, and the rate constants k_5 and k_{8a}, as given in Table 4. We could not measure k_{8a} directly, unlike the case of carbonyl compounds, so that we can only compare the ratio k_5/k_{8a}, but if we could assume tentatively that k_{8a} of nitromethane is equal to that of acetaldehyde, k_5 would be 3.4×10^6 sec^{-1}.

TABLE 5. SUMMARY OF PHOTOSTATIONARY STATE RATIO

Sensitizer	E_T (kcal/mol)	$([\mathrm{B}_{trans}]/[\mathrm{B}_{cis}])_{\mathrm{PSS}}$
$Hg(^3P_1)$	112.7	1.0[33]
Benzene	84.4	1.37[30]
Benzene	84.4	0.92[31,32]
Acetone	79—82	0.94[34]
Nitromethane	80	0.90

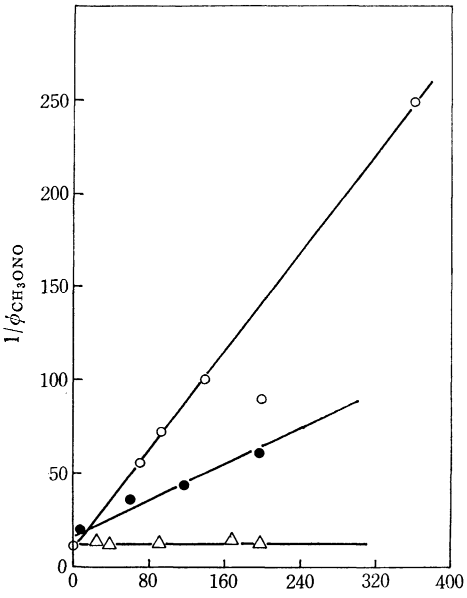


Fig. 5. Stern-Volmer plots of the quantum yield of methyl nitrite against the press. of quenchers.
○; *cis*-2-butene, ●; ethylene, △; CO_2

We investigated the change of quantum yield of methyl nitrite with the increase in the pressure of *cis*-2-butene. The Stern-Volmer plot of $1/\phi_{\mathrm{CH_3ONO}}$ against ethylene and *cis*-2-butene gives a good linear relationship (Fig. 5). The result is consistent with the following equation derived on the basis of the reaction mechanism we proposed.

$$\frac{1}{\phi_{\mathrm{CH_3ONO}}} = \frac{1}{\phi_T}\left(\frac{k_{9a}+k_{9b}}{k_{9b}}\right)\left(1+\frac{k_8[\mathrm{Q}]}{k_5}\right) \qquad (7)$$

The ratio k_5/k_8 is again calculated from the slope with the values of ϕ_T, and $(k_{9a}+k_{9b})/k_{9b}$, giving the value 2.0×10^{-2} mol/l for *cis*-2-butene and 5.8×10^{-2} mol/l for ethylene, respectively. The value for *cis*-2-butene is about 20% larger than that derived by the Cundall method from isomerization data. When the assumption and experimental errors are taken into account, both values may be in good agreement.

TABLE 6

	ϕ_T	k_5/k_{8a} (mol/l)	k_5 (sec^{-1})	k_8 (l/mol, sec)	$\frac{k_8\ (cis\text{-2-butene})}{k_8\ (\mathrm{CH_2{=}CH_2})}$
Nitromethane	0.6	1.7×10^{-2}	3.4×10^6	2×10^8	2.9
Acetone[24]	1.0	6×10^{-2}—6×10^{-4}	1.25×10^6	2×10^7—2×10^9 [a]	6.2
Acetaldehyde[25]	0.4	3—6×10^{-3}	6.2×10^5	1—2×10^8	

a) Depending on the amount of excess vibrational energy of triplet sensitizer ($2.5\times10^{10}\exp(-6400/\boldsymbol{RT})$ sec^{-1}).

---

33) R. J. Cvetanovic and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962).

34) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 5569 (1965).