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Studies of Photochemical Reactions Using Organic Photosensitizers. I. Benzene-Photosensitized Decomposition of Nitrous Oxide

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Benzene-photosensitized decomposition of nitrous oxide has been studied in a mercury-free reaction system. 2537 Å line of low-pressure mercury lamp was absorbed by benzene and the excitation energy of benzene was transferred to nitrous oxide by triplet-triplet energy transfer mechanism. Only N–O bond rupture of nitrous oxide has been observed, which is reasonable from energetic view point. The decomposition yield of the excited triplet state of nitrous oxide was estimated to be 15% and the triplet state seems to be less than 84 kcal/mol above the ground state.

In recent years a large number of works on photochemical reactions using organic photosensitizers have been reported. Most of the work, however, has been carried out on the reactions of organic compounds in liquid phase. Since the pioneer work of Dubois and Noyes[1] only a few studies have been reported about gas phase photochemical reactions involving chemical bond splitting caused by organic photosensitizers,[2,3] although a number of gas phase photochemical reactions have been studied by mercury-photosensitization and a review of these studies has been presented.[4]

It is easy to choose organic sensitizers of various triplet state energies. However, only a few sensitizers such as Hg and Cd are available as inorganic photosensitizers. Hammond *et al.* studied the energy dependecne of *cis-trans* isomerization reactions of olefins using various organic photosensitizers.[5]

In the present work, the photochemical decomposition of nitrous oxide was studied using benzene vapor as a sensitizer. Benzene is one of the most well-studied photosensitizer in photochemical reactions,[1,6,7] and the lowest triplet energy level is known to be 84 kcal/mol.[8]

Bond energies of nitrous oxide have been studied by electron impact method[9,10] and the linear structure of nitrous oxide has been given by infrared spectroscopy.[11]

Although nitrous oxide is a simple triatomic molecule, the cross section of nitrous oxide in quenching of the excited mercury atom (Hg 6^3P_1) is relatively high compared with other simple molecules.[4] Nitrous oxide was used as a quencher competing with ketene in the mercury-photosensitized reaction for the determination of the quenching cross section of ketene.[12]

From the study of thermal decomposition of nitrous oxide, N–O bond splitting seems to occur through a triplet state about 60 kcal/mol[13,14] above the ground state.

Since the absorption band of nitrous oxide lies in vacuum-ultraviolet region,[15,16] photosensitized decomposition of nitrous oxide would be observed by some organic sensitizers as well as by excited mercury atoms[17,18] if the excited triplet state of the organic sensitizers is higher than 60 kcal/mol.

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13) A. E. Stearn and H. Eyring, *ibid.*, **3**, 778 (1935).
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16) J. P. Doering and B. H. Mahan, *ibid.*, **34**, 1617 (1961).
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Experimental

For the study of benzene-photosensitized reaction, 2537 Å line of Toshiba FI-3S type low-pressure mercury lamp was used. The contribution from 1849 Å line was removed by Toshiba UVD-25 filter. In order to exclude the contribution from mercury-photosensitized decomposition of nitrous oxide, the reaction was carried out in a newly constructed, completely mercury-free reaction system and the pressure of the reaction system was measured by all-glass Bourdon pressure gauge. The reactor is a cylindrical quartz tube, 4 cm in diameter and 10 cm in length, and connected to the analyzing system. The reaction products were fractionated by cold traps and analyzed by Hitachi gas chromatograph Model K-53 and Hitachi RMU-5 mass spectrometer.

The sample of nitrous oxide used in the present work was 99.9% purity standard gas obtained from Takachiho Trading Co. The light intensity of the incident light into the reactor was measured by a ferrioxalate chemical actinometer.[19]

Results and Discussion

The decomposition of nitrous oxide was observed in the experiments of benzene-photosensitization of nitrous oxide. The reaction products which were not condensable in liquid nitrogen trap mainly consisted of nitrogen and carbon monoxide. The minor components in the noncondensable products were methane, hydrogen and sometimes a trace of oxygen.

Because of the difficulties in the identification of non-volatile species in the reaction products, material balance of the reaction was not measured.

Table 1 shows the N_2 and CO production under various benzene pressures for the same initial pressure of N_2O. The increase of N_2 formation with increase of the benzene pressure in the reaction system is seen in Fig. 1. This means that the amount of N_2 production corresponds to the number of photons absorbed by the sensitizer benzene.

Table 1. Benzene-photosensitized decomposition of nitrous oxide

Nitrous oxide pressure: 40.0 mmHg
Irradiation: 2537 Å, 60 min

C_6H_6 pressure (mmHg)	Product		N_2/CO	Quantum yield for N_2 formation
	N_2 (cc)	CO (cc)		
0	0.11×10^{-1}	—	—	—
5.2	0.44×10^{-1}	0.10×10^{-1}	4.4	2.60×10^{-2}
11.0	0.52×10^{-1}	0.10×10^{-1}	5.2	1.76×10^{-2}
13.0	0.62×10^{-1}	0.10×10^{-1}	6.2	1.75×10^{-2}
17.0	0.75×10^{-1}	0.15×10^{-1}	5.0	1.79×10^{-2}
22.5	0.94×10^{-1}	0.18×10^{-1}	5.2	1.90×10^{-2}
34.0	1.20×10^{-1}	0.36×10^{-1}	3.3	1.99×10^{-2}
35.0	1.12×10^{-1}	0.32×10^{-1}	3.7	1.84×10^{-2}
38.5	1.50×10^{-1}	0.45×10^{-1}	3.3	2.81×10^{-2}

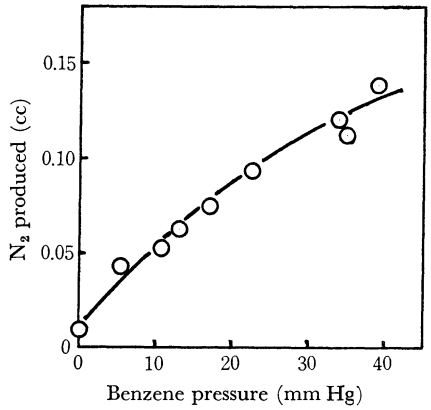

Fig. 1. The effect of benzene pressure on the amount of nitrogen formation.

Table 2 shows the N_2 and CO production with various N_2O initial pressure for the same benzene pressure. Here the apparent quantum yield presented in the table is the ratio of the mole number N_2 produced from N_2O to the number of photons absorbed by benzene.

The dissociation energies of N–N bond of nitrous oxide is 115 kcal/mol and N–O bond is 40 kcal/mol respectively,[9,10,20] and the excited triplet state energy of benzene is 84 kcal/mol.[8] It is quite reasonable, therefore, to expect that only N–O bond is split in the benzene-photosensitized decomposition of nitrous oxide. Nitric oxide was not produced and N_2 was the only nitrogen-containing product found in the reaction mixture after irradiation, which result is in agreement with the prediction of decomposition products of nitrous oxide.

While N_2 was produced by the decomposition of nitrous oxide in the present work, O_2 was not observed in almost any of the runs. Cvetanović observed that molecular oxygen was not formed when hydrocarbon was present in the reaction system of mercury-photosensitized decomposition of nitrous oxide.[17] It seems reasonable to suppose that oxygen atom, which was produced by N–O bond splitting in the benzene-photosensitized reaction of nitrous oxide, reacts rapidly with benzene before O_2 is formed by the recombination of oxygen atoms.[21] Carbon monoxide seems to be formed by the reaction of the oxygen atom from N_2O with benzene sensitizer. As seen in Tables 1 and 2, the ratio N_2/CO is larger than the stoichiometric value

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21) G. Boocock and R. J. Cvetanović, *Can. J. Chem.*, **39**, 2436 (1961).

1/1. This means that some of the oxygen atoms from N_2O molecules must have been missed in the analysis of the reaction products because of some non-volatile oxygen-containing products formed by the reaction of the oxygen atoms with benzene.[21]

The reaction scheme of the benzene-photosensitized decomposition of nitrous oxide may be presented as follows:

$$C_6H_6 + h\nu\ (2537\ \text{Å}) \longrightarrow C_6H_6^* \quad (1)$$

$$C_6H_6^* \longrightarrow C_6H_6 + h\nu' \quad (2)$$

$$C_6H_6^* \longrightarrow C_6H_6^{**} \quad (3)$$

$$C_6H_6^* + C_6H_6 \longrightarrow 2C_6H_6 \quad (4)$$

$$C_6H_6^{**} \longrightarrow C_6H_6 \quad (5)$$

$$C_6H_6^{**} + C_6H_6 \longrightarrow 2C_6H_6 \quad (6)$$

$$C_6H_6^{**} + N_2O \longrightarrow N_2O^{**} + C_6H_6 \quad (7)$$

$$N_2O^{**} \longrightarrow N_2 + O(^3P) \quad (8a)$$

$$N_2O^{**} \longrightarrow N_2O \quad (8b)$$

* and ** denote the excited state of molecule in singlet and triplet state, respectively. It is assumed that the reaction between the excited benzene and the reactant nitrous oxide can be neglected as in the case of previous workers.[1,2,6,7] The decomposition yield of nitrous oxide in the triplet state N_2O^{**} produced by the energy-transfer process (7) is expressed by $[k_{8a}/(k_{8a}+k_{8b})](N_2O^{**})$. When $k_{8a}/(k_{8a}+k_{8b})$ is replaced by n_t, the rate of N_2 formation is expressed as follows:

$$\begin{aligned} d(N_2)/dt &= n_t \cdot d(N_2O^{**})/dt \\ &= n_t k_7 (C_6H_6^{**})(N_2O) \\ &= \frac{n_t k_7 k_3 I(C_6H_6)(N_2O)}{(k_5+k_6(C_6H_6)+k_7(N_2O))(k_2+k_3+k_4(C_6H_6))} \end{aligned}$$

where, $I(C_6H_6)$ is the number of photons absorbed by benzene per unit time and k is the appropriate individual rate constant. Since the apparent quantum yield for N_2 formation Φ_t is expressed by $d(N_2)/dt \,/ I(C_6H_6)$, we obtain

$$\begin{aligned} \frac{1}{\Phi_t} &= \frac{1}{[d(N_2)/dt]/I(C_6H_6)} \\ &= \frac{1}{n_t}\left(1+\frac{k_2+k_4(C_6H_6)}{k_3}\right)\left(1+\frac{k_5+k_6(C_6H_6)}{k_7(N_2O)}\right) \end{aligned}$$

According to the results of the previous workers,

$$k_2/k_3 = 1/4^{7,22,23)}$$

$$k_2 + k_3 = 1.7\times10^6/\text{sec}^{24)}$$

and

$$k_4 = 4.6\times10^{-13}\ \text{cm}^3/\text{molecule sec}^{7)}$$

Table 2. Benzene-photosensitized decomposition of nitrous oxide

Benzene pressure: 35.0 mmHg
Irradiation: 2537 Å, 60 min

N_2O Pressure (mmHg)	Product N_2 (cc)	Product CO (cc)	N_2/CO	Quantum yield for N_2 formation
14.0	0.22×10^{-1}	—		0.36×10^{-2}
22.0	0.40×10^{-1}	0.08×10^{-1}	4.3	0.65×10^{-2}
25.0	0.64×10^{-1}	0.13×10^{-1}	4.9	1.05×10^{-2}
29.0	0.81×10^{-1}	0.21×10^{-1}	3.9	1.33×10^{-2}
35.0	0.91×10^{-1}	0.18×10^{-1}	5.0	1.47×10^{-2}
44.0	1.12×10^{-1}	0.32×10^{-1}	3.5	1.84×10^{-2}
53.0	1.47×10^{-1}	0.38×10^{-1}	3.9	2.41×10^{-2}
55.0	1.20×10^{-1}	0.36×10^{-1}	3.3	1.99×10^{-2}
65.0	1.57×10^{-1}	0.43×10^{-1}	4.3	2.57×10^{-2}

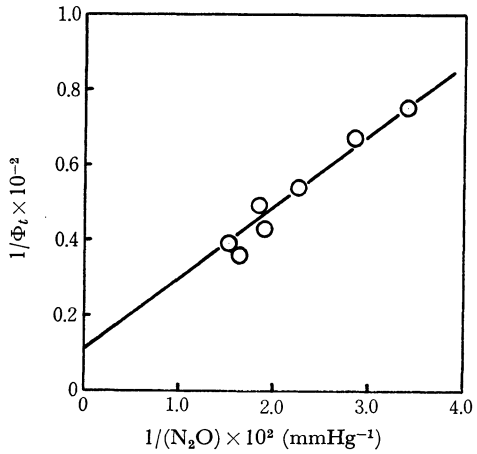

Fig. 2. Linear relation between $1/(N_2O)$ and reciprocal of apparent quantum yield for N_2 formation.

In the present work sensitizer benzene pressure was kept constant at 35.0 mmHg in every run listed in Table 2, thus

$$\frac{1}{\Phi_t} = \frac{c}{n_t}\left(1+\frac{k_5+k_6(C_6H_6)}{k_7(N_2O)}\right)$$

where the constant c denotes $\left(1+\frac{k_2+k_4(C_6H_6)}{k_3}\right)$ which was calculated using the numerical values of k_2, k_3, k_4 and (C_6H_6) mentioned above. The above equation shows the linear relation between $1/\Phi_t$ and $1/(N_2O)$. This is shown in Fig. 2 obtained from the experimental results in Table 2. From the intercept in Fig. 2, we obtain

$$c/n_t = 1.1\times10^1$$

Since the constant c is calculated to be 1.67, $n_t = k_{8a}/(k_{8a}+k_{8b})$ is evaluated to be

$$n_t = 0.15$$

We might propose that the decomposition yield of N_2O^{**} is 15%, since the material balance was not

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23) W. A. Noyes, Jr., and I. Unger, "Advances in Photochemistry," Vol. 4, ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York (1966), p. 50.

24) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961).

obtained from the analysis of the reaction products as mentioned before.

Since the excited singlet state of nitrous oxide lies in a vacuum-ultraviolet region shorter than 2537 Å, which is the wavelength of the light source for exciting benzene sensitizer in the present work, the energy transfer process (7) seems to be exclusive for exciting nitrous oxide under the present experimental conditions.

It has been pointed out that, in mercury-photosensitized reactions of the reactant molecule species having large quenching cross sections to excited mercury atoms, triplet-triplet energy transfer process is preferable to the direct attack mechanism.[25] Nitrous oxide has a large quenching cross section compared with other simple inorganic compounds and saturated hydrocarbons.[4,26] Considering the similarity of benzene-photosensitization with mercury-photosensitization, energy transfer process (7) for N_2O excitation is more plausible than the direct attack of excited benzene molecule on the nitrous oxide molecule.

Since N–O bond splitting has been observed by the benzene-photosensitized reaction of nitrous oxide in the present work, the excited triplet state of nitrous oxide in process (7) should be located less than 84 kcal/mol above the ground state, which is consistent with the results obtained in the thermal decomposition studies of nitrous oxide by previous workers[13,14] and also with those of the biacetyl-photosensitized reaction of nitrous oxide in which N_2 formation was observed by the present authors.[27] For more elaborate discussions about the triplet excited state of nitrous oxide assumed in the present work, however, reliable experimental evidence such as emission studies would be necessary.

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26) B. deB. Darwent and M. K. Phibbs, *J. Chem. Phys.*, **22**, 110 (1954).

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