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The Liquid-phase γ-Radiolysis of Benzene-Nitrous Oxide Mixtures

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The γ-radiolysis of the benzene-nitrous oxide liquid mixtures has been studied at room temperature and at 0°C, the mixing ratios covering almost all the range from pure benzene to pure nitrous oxide. Phenol was found to be one of the main products; its G-value is about a half of that of nitrogen at the lower concentration of nitrous oxide. Kinetic analysis shows that the G-values of electrons from benzene are 3.2 ± 0.2. An empirical equation for expressing the G-value of nitrogen from the benzene solution of nitrous oxide proposed by Hentz and Sherman (*J. Phys. Chem.*, **73**, 2676 (1969).) was examined. The agreement was very poor at higher concentrations of nitrous oxide. Possible reasons were discussed.

In recent years there has been much interest in the formulation of quantitative descriptions of the nonhomogeneous kinetics of charge scavenging in the liquid-phase radiolysis.[1–4] Warman, Asmus, and Schuler proposed an empirical equation for the charge scavenging and adduced much experimental evidence for the validity of this equation, especially in connection with the radiolysis of cyclohexane:[5]

$$G_s = G_{fi} + G_{gi}\frac{\sqrt{\alpha S}}{1+\sqrt{\alpha S}} \tag{I}$$

Here, G_s is the 100 eV yield of electrons or cations scavenged by an additive, the molarity of which is denoted by S. G_{fi} is the yield of free ion pairs; *i.e.*, these pairs escape from their mutual Coulombic field. G_{gi} is the yield of geminate-ion pairs, which are restrained in their mutual Coulombic field. The α parameter can be considered to be proportional to the specific rate of the charge-scavenging reaction. When nitrous oxide is used as an electron scavenger and when the G-value of nitrogen from the solution is used as a measure of the electron scavenging, Eq. (I) has to be modified, because the production of nitrogen from a hydrocarbon solution is believed to consist of two steps.[6] Hentz and Sherman discussed four possible mechanisms for the formation of nitrogen in a benzene solution.[7] The mechanism they preferred was the following:

$$e^- + N_2O \rightarrow N_2O^- \tag{1}$$

$$N_2O^- + C_6H_6 \rightarrow N_2 + C_6H_6O^- \tag{2}$$

$$C_6H_6O^- + N_2O \rightarrow N_2 + \text{residue} \tag{3}$$

In any mechanism, however, the formation of nitrogen has two origins, such as the reactions (2) and (3), both of which complete with neutralization. Therefore, if we use Eq. (I) as an analogy, the empirical equation for $G(N_2)$ should have the following form:

$$G(N_2) = 2G_{fi} + G_{gi}\frac{\sqrt{\alpha S}}{1+\sqrt{\alpha S}}\left(1+\frac{\sqrt{\beta S}}{1+\sqrt{\beta S}}\right) \tag{II}$$

Here, G_{fi}, G_{gi}, and S have the same meanings as in Eq. (I). The β parameter is for the reaction (3), the analog of α in the reaction (1). Hentz and Sherman used this equation to analyze their experimental results on the radiolysis of the benzene solution of nitrous oxide and thus estimated the values of G_{gi}, α, and β.

When comparing the radiolyses of cyclohexane and benzene solutions of nitrous oxide, the most remarkable difference observed is in the G-value of nitrogen; the $G(N_2)$ from the cyclohexane solution is more than twice that from the benzene solution at the same concentrations of nitrous oxide up to 0.5 mol/*l*.[8] A possible explanation of this is that the G-value of the electrons from benzene might be much smaller than that of those from cyclohexane. However, this is not likely because the W-values of these two compounds in the gas phase are believed to be not very different. Another explanation is that the ratio between the rate of the recombination reaction of geminate-ion pairs and the rate of the electron-scavenging reaction of nitrous oxide is much larger in benzene than in cyclohexane. If this is the case, the $G(N_2)$ from the benzene solution should approach the value obtained from the cyclohexane solution with an increase in the concentration of nitrous oxide to more than 0.5 mol/*l*.

Experimental

Tokyo Pure Chemical Co. benzene (spectro grade) was used as supplied. Since the G-values of the hydrogen (0.04) and biphenyl (0.08) were in good agreement with the reported values, further purification was not made. Nitrous oxide (Matheson Co. pure grade) was distilled bulb-to-bulb, and the head and tail fractions were rejected.

All the mixtures were sealed into small sampling glass tubes (about 3 m*l*) with a breakable seal attached. The amount of benzene was measured by a small pippet or a micro syringe, and that of nitrous oxide, volumetrically. The nitrous oxide concentrations at room temperature were calculated by using the Ostwald solubility coefficient of 3.8. At this temperature, more than 4 mol/*l* could not be attained because of the fragility of the breakable seal. At 0°C, however, almost all the mixing ratios could be obtained. At concentrations lower than 0.2 mol/*l*, the solution was crystallized. Several runs were made at the temperature of a dry

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[1] A. Mozumder, "Advances in Radiation Chemistry," Vol. 1, ed. by M. Burton and J. L. Magee, Wiley-Interscience, New York (1969), p. 1.

[2] J. M. Warman, K. -D. Asmus, and R. H. Schuler, *Adv. Chem. Ser.*, **82**, 25 (1968).

[3] G. R. Freeman, *Rad. Res. Rev.*, **1**, 1 (1968).

[4] S. Sato, This Bulletin, **41**, 304 (1968).

[5] J. M. Warman, K. D. Asmus, and R. H. Schuler, *J. Phys. Chem.*, **73**, 931 (1969).

[6] G. Scholes and M. Simic, *Nature*, **202**, 895 (1964).

[7] R. R. Hentz and W. V. Sherman, *J. Phys. Chem.*, **73**, 2676 (1969).

[8] S. Sato, R. Yugeta, K. Shinsaka, and T. Terao, This Bulletin **39**, 156 (1966).

ice-methanol mixture. In this case, solid benzene floated in the liquid nitrous oxide.

Samples were irradiated at their respective temperatures by ^{60}Co γ rays with a dose rate of 0.88×10^6 R/hr, usually for 4 hr. To analyze the gases noncondensable at the liquid-nitrogen temperature, the irradiated sample tubes were used to a conventional vacuum line, and after had been broken the seal, the gas in the two liquid nitrogen traps was collected by a Toepler pump and placed in a gas buret connected to a cuprous oxide furnace in order to combust the trace of hydrogen produced. In order to analyze the products in the solution, the seal was broken in the atmosphere, and a micro syringe was used to inject a small amount of the solution into the gas chromatographs (a 1-m dioctyl-phthalate column at 130°C and a 0.5-m alkyl-benzene-sulfonic-acid-sodium-salt column at 125°C). The quantitative estimation was made by comparing the peak areas with those of the prepared solutions. To ascertain the formation of phenol, a Millon reagent was also used. The yield calculated from the absorbance at 400 nm was in fair agreement with that estimated by gas chromatography.

Results

Tables 1 and 2 summarize the results obtained at room temperature. The G-value of nitrogen increased with the increase in the concentration of nitrous oxide, reached 6.74 at the highest concentration examined, and still showed a tendency to increase. The yields of phenol and biphenyl also increased with the increase in the nitrous-oxide concentration, but the yield of an unspecified product (probably hydrogenated biphenyl) stayed constant.

TABLE 1. G-VALUE OF NITROGEN FROM THE γ-RADIOLYSIS OF BENZENE SOLUTION OF NITROUS OXIDE AT ROOM TEMPERATURE[a]

N_2O mol/l	$G(N_2)$	N_2O mol/l	$G(N_2)$
0.118	1.37	1.30	4.30
0.119	1.26	1.37	4.41
0.203	1.87	1.54	4.82
0.313	2.16	1.70	4.95
0.615	3.16	1.81	5.01
0.965	3.70	2.01	5.00
1.01	3.92	3.04	6.06
1.27	4.28	4.64	6.74

a) Within experimental error, the G-values of nitrogen coincide with the following relation. $G(N_2)=3.78\sqrt{[N_2O]}$.

TABLE 2. G-VALUES OF PHENOL, BIPHENYL, AND UNSPECIFIED PRODUCTS[a] FROM THE γ-RADIOLYSIS OF BENZENE SOLUTION OF NITROUS OXIDE AT ROOM TEMPERATURE

N_2O mol/l	G-Value		
	Phenol	Biphenyl	Unspecified
0	0	0.08	0.06
0.366	1.50	0.51	0.11
0.568	1.48	0.33	0.09
0.753	2.10	0.57	0.13
0.955	1.82	0.42	0.08
1.15	2.00	0.47	0.08
1.70	2.46	0.68	0.10
2.09	2.56	0.63	0.08
3.37	3.96	0.91	0.09
4.52	4.00	0.99	0.05

a) The elution time on the gas-chromatograph corresponds to that of hydrogenated biphenyls.

The results obtained at 0°C are summarized in Tables 3 and 4. In these cases, the concentration was expressed by the mole fraction, because the liquid volume was substantially affected by the amount of nitrous oxide.

TABLE 3. G-VALUE OF NITROGEN FROM THE γ-RADIOLYSIS OF BENZENE-NITROUS OXIDE LIQUID MIXTURES AT 0°C

N_2O mol%	$G(N_2)$	N_2O mol%	$G(N_2)$
15.4	3.75	63.0	7.18
15.5	4.13	72.5	7.78
28.4	4.91	81.0	8.33
32.9	5.00	90.3	9.14
40.2	6.07	92.7	9.74
46.2	6.77	94.4	10.2
51.3	7.26		

TABLE 4. G-VALUES OF PHENOL, BIPHENYL, AND UNSPECIFIED PRODUCTS FROM THE γ-RADIOLYSIS OF BENZENE-NITROUS OXIDE LIQUID MIXTURES AT 0°C

N_2O mol/l	G-Value		
	Phenol	Biphenyl	Unspecified
19.4	2.07	0.40	0.05
21.8	2.30	0.38	0.05
28.8	2.26	0.49	0.04
41.6	2.91	0.55	0.05
45.9	3.01	0.54	0.05
52.3	2.92	0.50	0.03
54.7	3.01	0.48	0.02
61.1	2.94	0.48	0.02
66.9	2.78	0.48	0.02
68.7	2.96	0.48	0.02
70.9	2.96	0.41	0.02

In Fig. 1, the G-values of nitrogen and phenol are plotted as a function of the electron density of nitrous oxide. The G-value of nitrogen obtained at the temperature of dry ice-methanol is also plotted; it shows a linear dependence on the electron density of nitrous oxide.

Discussion

Formation of Phenol. In the study of the gas phase radiolysis of benzene-nitrous oxide mixtures, Rzad and Warman observed a very high yield of phenol formation (G ~40).[9] They proposed a chain mechanism involving the electron transfer from $C_6H_6O^-$ to nitrous oxide, a mechanism which corresponds

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[9] S. J. Rzad and J. M. Warman, *J. Phys. Chem.*, **72**, 3013 (1968).

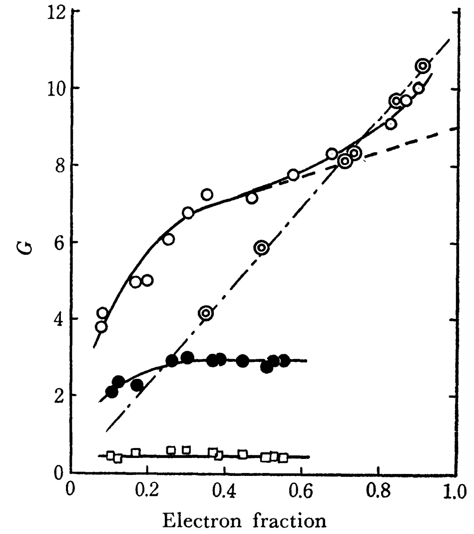

Fig. 1. G-Value of nitrogen (○), phenol (●), and biphenyl (□) obtained at 0°C and G-value of nitrogen (◎) at dry-ice temperature as a function of the electron density of nitrous oxide. Dashed line was tentatively drawn by connecting the G-value of nitrogen at around 0.5 in the electron density with $G_0=9$, which is the average used for the calculation of $g(N_2)$.

to the reaction (3) presented in the Introduction. To explain the present results, the chain mechanism is obviously not necessary. In place of the electron transfer, we tentatively assumed the following reactions:

$$C_6H_6O^- + N_2O \rightarrow N_2 + C_6H_6O_2^- \quad (3)$$

$$C_6H_6O_2^- + C_6H_6^+ \rightarrow C_6H_5OH + C_6H_6O \quad (4)$$

Here, C_6H_6O stands for the intermediate product of the reaction between benzene and an oxygen atom.

Boocock and Cvetanović investigated the reactions of oxygen atoms with benzene in the gas phase, using the mercury photosensitized decomposition of nitrous oxide as the source of oxygen atoms; they found that the yield of phenol formation is very much smaller than that expected from the yield of nitrogen.[10] The ratio in the yield of phenol to nitrogen formation was about 0.06. For the rest of the oxygen atoms, they found that carbon monoxide and polymers were formed. In the present study, carbon monoxide could not be observed. This may be attributed to the fact that the present experiment was performed in a liquid. The intermediate product, C_6H_6O, therefore, probably gives rise to only polymers. In fact, the formation of yellowish-white polymers was observed, though it was not analyzed.

As is shown in Tables 2 and 4, the yield of biphenyl increased with the increase in the concentration of nitrous oxide. This increase may be explained by the following reactions:

$$C_6H_6O^* \rightarrow C_6H_5 + OH \quad (5)$$

$$2\,C_6H_5 \rightarrow C_6H_5\text{-}C_6H_5 \quad (6)$$

Here, the asterisk denotes the excited state which is the precursor of C_6H_6O in the reaction (4).

Formation of Nitrogen. The gas-phase radiolysis of nitrous oxide has been investigated by many groups of investigators, but the mechanism of the formation of nitrogen has not yet been established in detail.[11,12] For the liquid phase, only one report by Robinson and Freeman could be found in the literature.[13] According to their tentative reaction mechanism, the G-value of ionization is 3.0, and that of excitation, which results in the decomposition into N_2 and O, is 6.4. Our present results are compatible with their mechanism. As may be seen in Fig. 1, when the electron fraction of nitrous oxide is in the range from 0.6 to 0.9, the G-values of nitrogen obtained at 0°C are a little smaller than those obtained at the dry-ice temperature. At this temperature, benzene and nitrous oxide probably decompose independently, because the system is not homogeneous. The deviation of $G(N_2)$ from the linearity obtained at the dry-ice temperature may be explained by the charge-transfer reaction from N_2O^+ to benzene. The ionization potential of nitrous oxide in the gas phase has been reported to be 12.9 eV, and that of benzene, to be 9.5 eV. This type of charge transfer may be completed at electron densities down to 0.6 in Fig. 1. If this reasoning is correct, the formation of nitrogen below 0.6 in the electron density of nitrous oxide should be explained by the following two types of reactions. One is the reaction initiated by the electron scavenging of nitrous oxide, which has already been discussed in the Introduction; the other is the non-ionic reaction of nitrous oxide, which may be described as follows:

$$N_2O \rightsquigarrow N_2 + O \quad (7)$$

The oxygen atoms produced in this reaction may react with benzene and produce a polymer, as has been discussed. This mechanism matches the observation that the G-value of phenol becomes saturated as the concentration of nitrous oxide increases, while in the same range of nitrous oxide concentration the G-value of nitrogen still has a tendency to increase.

Another possible non-ionic reaction forming nitrogen is the benzene sensitized decomposition of nitrous oxide. In this respect, we have recently examined the benzene-photosensitized decomposition of nitrous oxide in a cyclohexane solution. The light source used was a low-pressure mercury lamp. The quantum yield of the decomposition was very small (about 0.005). This result does not necessarily mean that the benzene-sensitized decomposition is negligibly small in the radiolysis, because highly excited states of benzene, which may be formed in the radiolysis but not in the photolysis, might play a role in the decomposition of nitrous oxide. This possibility, therefore, cannot be completely ruled out by the present experiment.

Nitrogen Resulting from the Electron Scavenging of Nitrous Oxide. In order to apply the empirical equation

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

[11] J. A. Hearne and R. W. Hummel, *Rad. Res.*, **15**, 254 (1961).

[12] S. Takao, S. Shida, Y. Hatano, and H. Yamazaki, This Bulletin **41**, 2221 (1968).

[13] M. G. Robinson and G. R. Freeman, *J. Phys. Chem.*, **72**, 1394 (1968).

(II) to the present data, we have to discriminate the G-value of the nitrogen produced by the electron scavenging from the value of that produced by other processes. A tentative calculation has been made by using the following relation:

$$G(N_2) = \varepsilon_B g(N_2) + \varepsilon_{N_2O} G_0$$

Here, $g(N_2)$ is the G-value of nitrogen resulting from the reaction initiated by the energy absorbed by benzene, and G_0 is the G-value of nitrogen from pure liquid nitrous oxide, excluding the contribution of N_2O^+. ε_B and ε_{N_2O} are the electron densities of benzene and nitrous oxide respectively. As the value of G_0, we had to take a wide range of values, from 8 to 10, because of the inaccuracy of the data, as is shown in Fig. 1. However, the calculated $g(N_2)$ values were not so scattered, as is shown in Fig. 2. The asymptotic value obtained at high concentrations of nitrous oxide ranges from 6.2 to 6.8. If the contribution from the benzene-sensitized decomposition can be disregarded, this value should be equal to twice that of the G-value of the electrons from benzene.

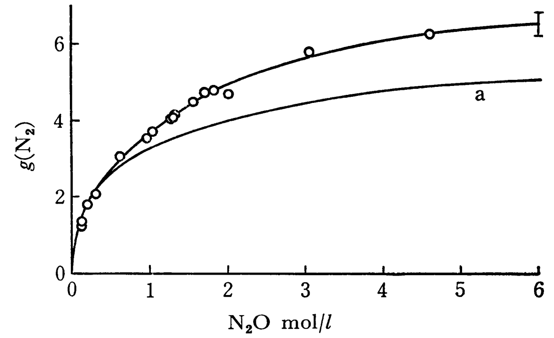

Fig. 2. G-Value of nitrogen formation initiated by the energy absorbed by benzene at room temperature as a function of the concentration of nitrous oxide. The curve a) is drawn by using Eq. (II).

The curve a) in Fig. 2 was drawn by using Eq. (II), with $G_{gi}=3.9$, $\alpha=0.7$ l/mol, and $\beta/\alpha=50$, according to the method of Hentz and Sherman.[7] The agreement was obviously very poor. We tried various combinations of the values for G_{gi}, α, and β, but as long as Eq. (II) was used, a successful adjustment could not be made. If Eq. (II) correctly expresses the result of the electron scavenging of nitrous oxide, the disagreement might be due to a neglect of the benzene-sensitized decomposition of nitrous oxide. However, the G-value of electrons estimated above, 3.2±0.2, is a little smaller than that to be expected from the W-value of benzene in the gas phase (~25 eV); *i.e.*, as far as the G-value of nitrogen is concerned, it is not necessary to take the contribution of the benzene-sensitized decomposition of nitrous oxide into account.

In connection with the G-value of electrons from benzene, the G-value of phenol at 0°C is suggestive; it does not exceed 3, even at the highest concentration of nitrous oxide examined. If the mechanism of the formation of phenol is that proposed above, the G-value of phenol should be nearly equal to that of the electrons scavenged by nitrous oxide. This, however, is not conclusive, either, because of the uncertainty of the reaction mechanism.

Although the validity of Eq. (I) is evidenced by many experimental results,[14] this equation itself has shortcomings when it is applied to higher concentrations of scavengers; experimentally, the value of $[S]$ cannot exceed that of the pure state, which is usually less than 10 mol/l for most of the solutes. Therefore, since α is 0.7 l/mol in the case of benzene, the $\sqrt{\alpha S}(1+\sqrt{\alpha S})^{-1}$ fraction is less than 0.8. Even in the case of $\alpha=16$ l/mol, which has been reported in the study of the electron scavenging of methyl bromide in the radiolysis of cyclohexane[2], the above fraction is 0.93. In other words, the G_{gi} estimated by using Eq. (I) or (II) can never be observed experimentally.

In the formulation of the non-homogeneous kinetics of charge scavenging, it is usually assumed, for the convenience of the theoretical treatment, that only one ion pair exists in a spur. Even Eq. (I) is based on the same assumption, though it is very empirical.[4] However, it is well known that the formation of multi-ion pairs in a spur is not negligibly small.[15] Therefore, when a high concentration of scavenger is used, the contribution of such ion pairs cannot be ignored. The large deviation of the experimental data from the empirical equation shown in Fig. 2 might be due to such a neglect. For a complete interpretation, further investigation is obviously desired.

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[14] S. J. Rzad, P. P. Infelta, J. M. Warman, and R. H. Schuler, *J. Chem. Phys.*, **52**, 3971 (1970).

[15] W. J. Beekman, *Physica*, **15**, 327 (1949).