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Energy Transfer in the γ-Irradiated Benzene Solutions of Carbonyl Sulfide, Nitrous Oxide, and Carbon Dioxide

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The γ-radiolysis of benzene solutions containing carbonyl sulfide, nitrous oxide, and carbon dioxide has been investigated at room temperature and at 0°C. Carbonyl sulfide was shown to be an effective electron scavenger and to give carbon monoxide as the product. By comparing the solute concentration dependences of $G(N_2)$ and $G(CO)$, it was concluded that the collision of secondary electrons with benzene does not efficiently produce the first excited singlet state, the G-value of which is less than 0.2 if it is produced at all. The concentration dependences of the $G(CO)$ and G(phenol) from the benzene solution of carbon dioxide also suggested that the superexcited state or the highly-excited state of benzene is too short-lived to transfer its energy to the solute.

When a benzene solution containing a small amount of a solute is irradiated by γ-rays, the solute molecules are subject to the attack of active species produced in the solvent and an "energy transfer from solvent to solute" occurs. Various mechanisms have been proposed for this energy transfer. The mechanisms may be classified into three categories. (1) The real energy transfer. The active species in this case are the first excited singlet ($^1B_{2u}$) and the lowest teiplet state ($^3B_{1u}$) of benzene. These states may be formed by the neutralization of benzene cations or by the direct excitation of secondary electrons. This type of energy transfer has been studied by many photochemists.[1,2] Our laboratory has also studied this type of energy transfer and shown that the benzene-photosensitized *cis-trans* isomerization of butene-2 in cyclohexane occurs through the triplet-triplet energy transfer when the concentration of the solute is less than 10^{-2} mol/*l*,[3] and that the benzene photo-sensitized decomposition of carbonyl sulfide through the singlet-singlet energy transfer.[4] (2) Ionic reactions. The active species in this case are electrons and benzene cations, whose reactions have been studied as an important subject of radiation chemistry. An example is the nitrogen formation from a γ-irradiated benzene solution of nitrous oxide.[5,6] It is believed that this reaction is initiated by the electron capture of nitrous oxide. As an example of the reaction of benzene cations, the formation of anisole in the γ-irradiated benzene-methanol mixture may be taken.[7] (3) The energy transfer from the superexcited state of benzene. This process has not been established by direct evidence, but its possibility has been discussed by theoretical radiation chemists.[8] Recently, Voltz quoted our data on the quenching effect of nitrous oxide on the scintillation from the *p*-terphenyl-benzene system as an example of this type of energy transfer.

The present paper will report the results of the γ-radiolysis of benzene solutions of carbonyl sulfide,

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[1] 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 and London, (1966), p. 49.

[2] P. J. Wagner and G. S. Hammond, *ibid.*, Vol. 5, (1968), p. 21.

[3] S. Sato, H. Kobayashi, and K. Fukano, *Kogyo Kagaku Zasshi*, **72**, 209 (1969).

[4] S. Sato, H. Miyamoto, S. Hirokami, and S. Tsunashima, This Bulletin, **45**, 754 (1972).

[5] S. Sato, R. Yugeta, K. Shinsaka, and T. Terao, *ibid.*, **39**, 156 (1966).

[6] S. Hirokami, S. Shishido, and S. Sato, *ibid.*, **44**, 1511 (1971).

[7] J. A. Ward and W. H. Hamill, *J. Amer. Chem. Soc.*, **89**, 5116 (1967).

[8] R. Voltz, "Progress and Problems in Contemporary Radiation Chemistry," Vol. 1, ed. by Teply, (1971), p. 139.

nitrous oxide, and carbon dioxide and will discuss the reaction mechanism for the formation of the products. The discussion will inevitably include the energy trasfer described above.

Experimental

Tokyo Kagaku Seiki Co. benzene (purest grade) was used as supplied. Further purification was not made.[6] The carbonyl sulfide (Merck Co.), nitrous oxide (Matheson Co.), and carbon dioxide (Takachiho Chemical Co.) were distilled bulb-to-bulb, and the head and tail fractions were rejected.

All the mixtures were sealed into small sampling tubes (about 3 m*l*) with a breakable seal attached. The subsequent procedure was the same as that reported in a previous paper.[6] Ostwald's solubility coefficients of carbonyl sulfide and nitrous oxide in benzene at room temperature are 12.5 and 3.8 respectively.

The samples were irradiated by ^{60}Co γ-rays at a dose rate of about 0.8×10^6 R/hr. In order to analyze the gases noncondensable at the temperature of liquid nitrogen, a Toepler pump with a gas buret and a cuprous oxide furnace attached was used. For the analysis of the products in the solution, we made use of a gas chromatograph, the column of which was 1-m dioctylphthalate at 130°C.

Results

COS–Benzene System. Table 1 shows the G-values of carbon monoxide and hydrogen as a function of the concentration of COS in benzene. The presence of the benzenethiol as one of the products could be detected by gas chromatography. However, the G-value at the COS concentration of 0.6 mol/*l* was as low as 0.12. No other products could be detected.

Since the dependence of G(CO) on the concentration of COS was very similar to that of $G(N_2)$ on the concentration of N_2O, as reported in a previous paper,[6] the radiolysis at 0°C was carried out for the sake of comparison, for at that temperature any ratio of COS to benzene can be obtained. The result is shown in Fig. 1, along with the $G(N_2)$ from the benzene solution of N_2O. Within the limit of experimental error, the two series of measurements coincide with each

TABLE 1. G-VALUES OF CO AND H_2 FROM THE BENZENE SOLUTION OF COS

COS mol/*l*	G(CO)	$G(H_2)$	COS mol/*l*	G(CO)	$G(H_2)$
0.0053	0.206	—	0.420	3.31	—
0.0078	0.567	—	0.472	3.45	0.032
0.0108	0.567	—	0.558	3.58	—
0.0113	0.591	0.036	0.562	3.67	—
0.0315	1.22	—	0.938	4.06	—
0.0570	1.47	0.033	1.07	4.62	—
0.0955	1.96	0.043	1.26	4.69	0.034
0.123	2.13	0.032	1.54	4.96	—
0.156	2.17	0.038	1.70	4.92	—
0.210	2.40	—	2.04	4.97	—
0.256	2.74	0.034	2.22	5.61	—
0.404	3.46	—	3.34	5.52	—
0.410	3.38	—	4.23	6.07	—

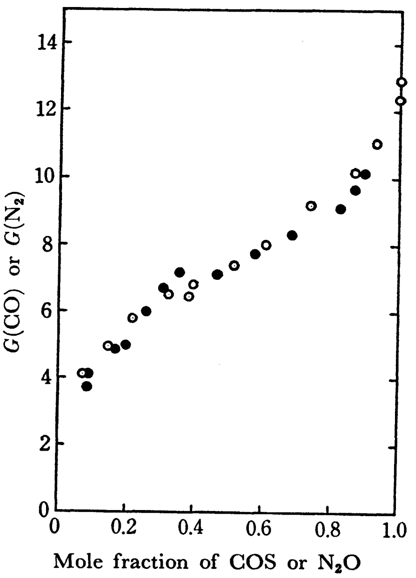

Fig. 1. G-values of CO and N_2 from the liquid phase mixtures of benzene-COS and benzene-N_2O at 0°C.
○: CO, ●: N_2

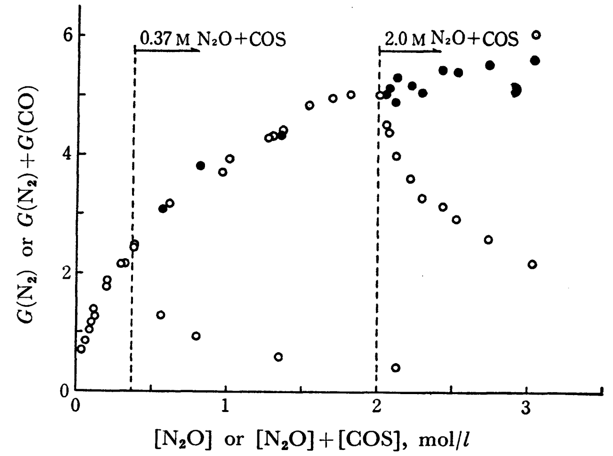

Fig. 2. G-values of N_2 from the benzene solution of N_2O at room temperature and the effect of the addition of COS.
○: $G(N_2)$, ●: $G(N_2)+G$(CO)

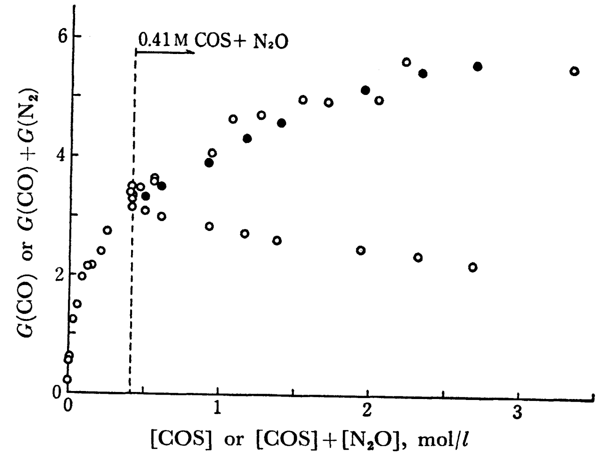

Fig. 3. G-values of CO from the benzene solution of COS at room temperature and the effect of the addition of N_2O.
○: G(CO), ●: $G(N_2)+G$(CO)

other.

COS–N_2O–Benzene System. In order to study the competition of COS and N_2O as electron scavengers, benzene solutions containing the two solutes were γ-irradiated. Figures 2 and 3 show the results. Some of the results in Fig. 2 have already been reported.[9] In each figure, it is noticeable that the sum of G(CO) and $G(N_2)$ at a certain concentration of $[COS]+[N_2O]$ is almost equal to the G(CO) or $G(N_2)$ value obtained at the same concentration of COS or N_2O.

CO_2–Benzene System. In place of COS and N_2O, CO_2 was also used as a solute. Figure 4 shows the G-values of CO, phenol, and biphenyl as a function of the mole fraction of CO_2. The temperature was 0°C; no CO_2 mole fraction higher than 0.9 could be attained because of the fragility of the breakable seal attached to the reaction vessel.

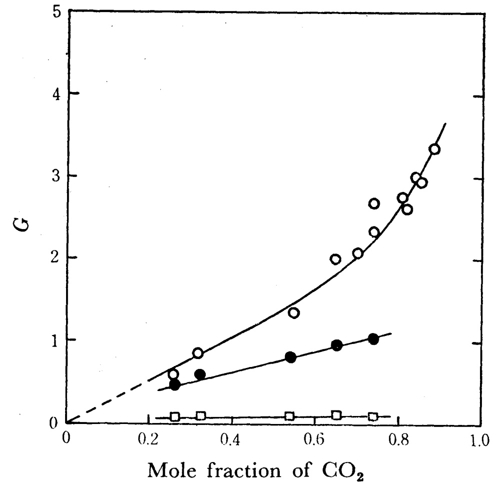

Fig. 4. G-values of CO, phenol, and biphenyl from the liquid phase mixture of benzene-CO_2.
○: CO, ●: phenol, □: biphenyl

Discussion

In the previous paper on the γ-radiolysis of the benzene solution of N_2O,[6] the reactions initiated by the electron capture of N_2O were described as follows:

$$e^- + N_2O \rightarrow N_2 + O^- \tag{1}$$

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

$$C_6H_6O^- + N_2O \rightarrow N_2 + C_6H_6O_2^- \tag{3}$$

$$C_6H_6O_2^- + C_6H_6^+ \rightarrow C_6H_6O + C_6H_5OH \tag{4}$$

As was stated in the Results section, the behavior of COS as the solute in the γ-irradiated benzene solution was very similar to that of N_2O. Therefore, the reactions of COS may be written as follows:

$$e^- + COS \rightarrow CO + S^- \tag{5}$$

$$S^- + C_6H_6 \rightarrow C_6H_6S^- \tag{6}$$

$$C_6H_6S^- + COS \rightarrow CO + C_6H_6S_2^- \tag{7}$$

$$C_6H_6S_2^- + C_6H_6^+ \rightarrow 2\,C_6H_6 + S_2 \tag{8}$$

In Reaction (8), the formation of benzenethiol was not assumed, because the G-value of this compound was very small. The product, S_2, in this reaction probably polymerizes to S_8.[10] When the two solutes, N_2O and COS, are present together in a solution, the following two reactions must be taken into account for the formation of CO and N_2:

$$C_6H_6O^- + COS \rightarrow CO + C_6H_6OS^- \tag{9}$$

$$C_6H_6S^- + N_2O \rightarrow N_2 + C_6H_6SO^- \tag{10}$$

As is shown in Fig.2, when COS is added to the benzene solution containing N_2O, the $G(N_2)$ rapidly decreases with the increase in the COS concentration, while the sum of $G(N_2)$ and G(CO) is almost equal to the $G(N_2)$ obtained at the N_2O concentration corresponding to $[COS]+[N_2O]$. The reverse situation is shown in Fig. 3, where N_2O is added to the COS–benzene solution. In this case, the decrease in G(CO) with the concentration of added N_2O is not so rapid as the decrease in $G(N_2)$ on the addition of COS to the N_2O solution. These results may be explained as follows.

The electrons ejected in the solution are captured by N_2O or COS, the rate constants of which may be almost equal.

$$k_1 = k_5 \tag{I}$$

Otherwise, the curves for $G(N_2)+G(CO)$ in Fig. 2 and 3 should differ considerably from each other. On the other hand, the second steps of the formation of N_2 and CO are strongly dependent upon the rate constants; $k_3<k_9$ and $k_{10}<k_7$.

For the further analysis of these data, we may tentatively divide the G-values of noncondensable gases into two parts:

$$\begin{aligned} G(N_2) &= G_1(N_2) + G_2(N_2) \\ G(CO) &= G_1(CO) + G_2(CO) \end{aligned} \tag{II}$$

Here, G_1 denotes the G-value of the noncondensable gas resulting from Reaction (1) or (5), and G_2, that resulting from Reactions (3) and (10) or (7) and (9). Therefore, the following relation should hold:

$$\frac{G_1(N_2)}{G_1(CO)} = \frac{k_1[N_2O]}{k_5[COS]} = \frac{[N_2O]}{[COS]} \tag{III}$$

Since the solute concentration under present consideration is higher than 0.4 mol/l, the $C_6H_6O^-$ and and $C_6H_6S^-$ species may react further with the solutes before being neutralized. In other words, all the electrons captured by scavengers will produce two molecules of N_2 or CO:

$$G(N_2) + G(CO) = 2\{G_1(N_2) + G_1(CO)\} \tag{IV}$$

Then, if the $[N_2O]/[COS]$ ratio is known, we can calculate $G_2(N_2)$ and $G_2(CO)$.

On the other hand, if we can assume:

$$k_3/k_9 = k_{10}/k_7 = K \tag{V},$$

then we can easily derive the following equation:

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[9] S. Hirokami, S. Shishido, and S. Sato, This Bulletin, **43**, 973 (1970).

[10] H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," Vol. 4, ed. by W. A. Noyes, Jr., G. B. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York and London, (1966), p. 143.

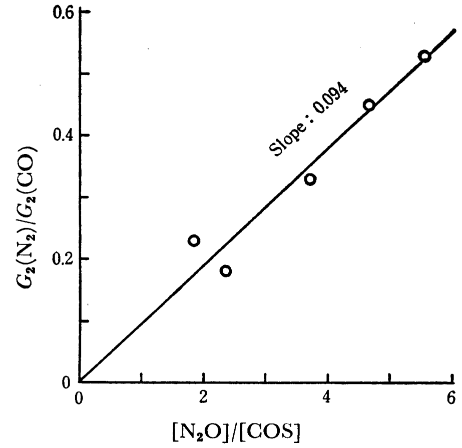

Fig. 5. $G_2(N_2)/G_2(CO)$ as a function of $[N_2O]/[COS]$ calculated from Fig. 2.

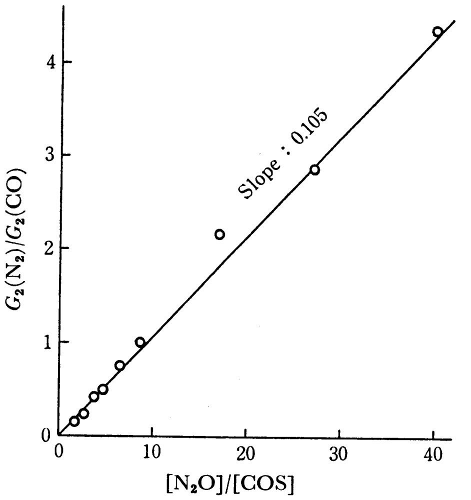

Fig. 6. $G_2(N_2)/G_2(CO)$ as a fuuction of $[N_2O]/[COS]$ calculated from Fig. 3.

$$\frac{G_2(N_2)}{G_2(CO)} = K\frac{[N_2O]}{[COS]} \qquad \text{(VI)}$$

Figure 5 was drawn from the data in Fig.2, and Fig.6, from those in Fig.3. Obviously, we could obtain the linear relationships expected from Eq. (VI) and a constant slope:

$$K = 0.10 \pm 0.005 \qquad \text{(VII)}$$

The agreement of these two slopes seems to support the reasoning presented above. We have tried to a more general relationship between the G-values of N_2 and CO, and the concentrations of N_2O and COS on the basis of the proposed reaction scheme, but no simple equations have so far been derived because of the inhomogeneous kinetics involved in the neutralization processes of ions in the system.

So far, we have stressed that the two curves of $G(N_2)+G(CO)$ in Figs. 2 and 3 are similar: however, a detailed comparison reveals that the two curves do not coincide with each other exactly especially, at the lower concentrations of the solutes. In the previous paper,[6] we showed that the $G(N_2)$ from the N_2O benzene solution is proportional to the square root of the N_2O concentration up to 2 mol/l:

$$G(N_2) = 3.78\sqrt{[N_2O]} \qquad \text{(VIII)}$$

By using this relation, the difference between $G(N_2)$ in Fig. 2 and G(CO) in Fig. 3 was plotted as a function of the concentration of the solute. The results are shown in Fig.7. This difference may be partly due to the difference in the electron-scavenging efficiencies of N_2O and COS, but we believe that the main part result from the difference between the two compounds in sensitivity to the excited state of benzene. As has already been reported, N_2O and COS show quite different behaviors in the benzene-photosensitization; that is, the quantum yield of the formation of N_2 in the benzene-photosensitized decomposition of N_2O in cyclohexane is very small (<0.01 at 0.06 mol/l N_2O),[6] while COS is easily decomposed into CO and S by the benzene photo-sensitization ($\phi_{CO}=0.4$ at 0.06 mol/l COS).[4] Therefore, if the first excited singlet state of benzene ($^1B_{2u}$) is efficiently formed by the direct excitation of the secondary electrons in the radiolysis of the benzene solution, the $G(N_2)$ curve in Fig.2 should differ considerably from the G(CO) curve in Fig. 3. In fact, the difference is small, as is shown in Fig. 7, and may be explained as follows. The electrons not scavenged by COS return to the parent benzene cations and produce the excited states of benzene, which can decompose COS. This process may be schematically described as follows:

$$e^- + C_6H_6^+ \rightarrow C_6H_6^*(^1B_{2u}) \qquad (11)$$

$$\searrow C_6H_6^{**}(^3B_{1u} \text{ or others}) \qquad (12)$$

$$C_6H_6^* + COS \rightarrow C_6H_6 + CO + S \qquad (13)$$

If this reasoning is correct, the following conclusion can be drawn—that the secondary electrons produced in the γ-radiolysis of benzene do not produce the first excited singlet state of benzene by direct collision. This statement, of course, does not mean that collisions of the secondary electrons with benzene give no electronically-excited states of benzene. Rather, the truth is probably that a large number of the electronically-excited states are produced, but their states are so high compared with the $^1B_{2u}$ state that the

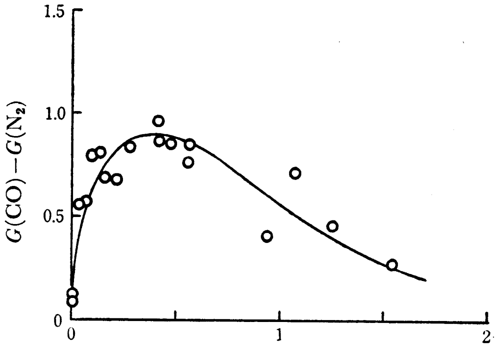

Fig. 7. The difference between G(CO) and $G(N_2)$ as a function of the concentration of the solute.

conversion to the $^1B_{2u}$ state is not efficient.[11] Although the experimental error precludes an accurate estimation, the G-value of the $^1B_{2u}$-state benzene produced directly by the collision of secondary electrons cannot be higher than 0.2, if it is produced at all.

Fighure 4 shows the G-values of CO, phenol, and biphenyl from the benzene solution of CO_2. The yields of CO and phenol are almost linearly dependent upon the concentration of CO_2 at its lower concentrations. This suggests that CO and phenol are produced by the reactions of the active species formed from CO_2. It is known that oxygen atoms in the ground state do not efficiently produce phenol in the reaction with benzene. One possible mechanism for the formation of phenol, therefore is as follows:

$$\begin{aligned}
&C_6H_6 \rightsquigarrow C_6H_6^+ + e^- \\
&CO_2 \rightsquigarrow CO + O \\
& \rightsquigarrow CO_2^+ + e^- \\
&O + e^- \rightarrow O^- \\
&O^- + C_6H_6 \rightarrow C_6H_6O^- \\
&CO_2^+ + C_6H_6 \rightarrow CO_2 + C_6H_6^+ \\
&C_6H_6^+ + C_6H_6O^- \rightarrow C_6H_5OH + C_6H_6
\end{aligned}$$

This reaction scheme is very tentative, but it explains the linear dependence of G(CO) and G(phenol) on the CO_2 concentration.

Recently, much interest has been taken in the superexcited state produced in the radiolysis.[12] According to Voltz's estimation,[8] the energy transferred from the superexcited state or highly-excited state of aromatic compounds in the liquid phase is, very roughly, 20 eV. Moreover, he quoted our data regarding the quenching effect of N_2O in the scintillation from the *p*-terphenyl-benzene system as an example of the energy transfer from the superexcited state or the highly-excited state of benzene to the solute.[8] However, if the energy of 20 eV is transferred from the superexcited state of benzene to the solute, CO_2 should be decomposed as was N_2O if the solute used is CO_2 instead of N_2O. Figure 4 obviously shows that this is not likely. Therefore, it may safely be said that superexcited state or the highly-excited state of benzene is too short-lived to transfer its energy to the solute molecules.

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[11] C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963).

[12] Y. Hatano, S. Shida, and S. Sato, This Bulletin, **41**, 1120 (1968).