The γ-Ray Induced Oxidation of Aromatic Hydrocarbons in Liquid Dinitrogen Oxide

Hidetoshi Karasawa, Rei Yugeta, and Shin Sato*
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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The γ-ray induced oxidation of aromatic hydrocarbons has been studied in liquid dinitrogen oxide, mainly at -18 °C. Various mixing ratios of dinitrogen oxide and four aromatic hydrocarbons have been examined. The main oxygen-containing products observed were the corresponding phenols and benzyl alcohols. The kinetic analysis showed that ionic species, probably N_2O^- ions, are the main precursors at low mole fractions of dinitrogen oxide and that oxygen atoms become important with an increase in the mole fraction. 1-Butene was used as a scavenger of oxygen atoms. The following rate constant ratios were obtained for the reactions of oxygen atoms and N_2O^- ions: $k(\text{O}+\text{toluene})/k(\text{O}+\text{1-butene})=0.02$, $k(\text{O}+\text{toluene})/k(\text{O}+\text{benzene})=2.0$, and $k(\text{N}_2\text{O}^-+\text{1-butene})/k(\text{N}_2\text{O}^-+\text{toluene})=2.5$. The relative rates for the formation of the corresponding phenols and benzyl alcohols through ionic reactions from aromatic hydrocarbons were obtained as follows: benzene, 1.0; toluene, 2.5; *p*-xylene, 2.2; 1,3,5-trimethylbenzene, 3.1. These values are quite different from the relative rate constants of the reactions of oxygen atoms with these aromatic hydrocarbons.

Recently much interest has been attracted to the γ-ray-induced oxidation of hydrocarbons in liquid carbon dioxide and dinitrogen oxide. The oxidizing species produced in the γ-radiolysis of a carbon dioxide solution are mainly oxygen atoms.[1-3] In a previous paper,[4] we reported on the reactions between oxygen atoms and several olefins in liquid carbon dioxide and discussed the relative rate constants of these reactions and the difference between gas- and liquid-phase reactions.

On the other hand, the oxidizing species produced in the γ-radiolysis of liquid dinitrogen oxide include not only oxygen atoms, but also N_2O^- ions and/or $N_2O_2^-$ ions.[5] When cyclohexene was used as a reactant, these oxidizing species formed different oxygen-containing products; oxygen atoms produced cyclohexene oxide and cyclohexanone, while ionic species led to the formation of cyclohexanol, 2-cyclohexenol, and probably water.

Aromatic hydrocarbons were also used as reactants in γ-ray-induced oxidation in liquid carbon dioxide.[6,7] The main products observed were the corresponding phenol. Sakurai *et al.* discussed the reaction mechanism and concluded that the oxidizing species are oxygen atoms when the mole fraction of carbon dioxide is higher than 0.9.[8-10]

About ten years ago, we studied the liquid-phase γ-radiolysis of benzene in the presence of dinitrogen oxide and measured the *G*-value of phenol.[11] The initial oxidizing species were concluded to be O^- or N_2O^- ions; *i.e.*, phenol seems to be formed from both oxidizing species, oxygen atoms and ionic species.

The present experiment attempted to confirm the formation of phenols in the reactions of ionic species with aromatic hydrocarbons and to obtain the relative rate constants of these reactions.

Experimental

The experimental procedure was the same as that described in a previous paper.[4] The dinitrogen oxide, purchased from the Takachiho Shoji Co., contained no detectable impurities; this was confirmed by means of a gas-chromatograph equipped with a 5-m dimethyl sulfolane column of 20% w/w on celite. The 1-butene, benzene (Merck Co.), toluene, *p*-xylene, and 1,3,5-trimethylbenzene (Tokyo Kasei Co.) were used after thorough degassing.

About 1 cm^3 of a liquid containing various mixing ratios of N_2O and hydrocarbons was irradiated with ^{60}Co γ-rays at -18 °C (sodium chloride-ice slush) except when otherwise stated. The dose was estimated by Fricke dosimetry on the assumption of a proportionality between the electron density and the dose.

The amount of the noncondensable product at 77 K was measured with a Toepler pump and a gas burrette. The other products were analyzed by gas-chromatography after the excess dinitrogen oxide had been removed at -78 °C. The columns used for the analysis were a 2-m Cresol-3M column (Nishio Kogyo Co.) for phenols and benzyl alcohols, and 2-m PEG-1500 and 2-m DNP columns (Gaschro Kogyo Co.) for 1-butene oxide, butanal, and 2-butanone.

Results and Discussion

Toluene–1-Butene–N_2O System. The main products observed in the γ-radiolysis of the mixture of toluene, 1-butene, and dinitrogen oxide are nitrogen, three isomeric cresols, benzyl alcohol, 1-butene oxide, butanal, and 2-butanone. The *G*-values of these products are shown in Figs. 1, 2, and 3 as functions of the electron fraction (ε) of dinitrogen oxide. It is noticeable that the electron-fraction dependence of cresols and benzyl alcohol is quite different from that of 1-butene oxide, butanal, and 2-butanone. This suggests that the two products, the product from toluene and that from 1-butene, are different in the mechanism of their formation.

The Precursor of 1-Butene Oxide. It is now well known that the reaction of oxygen atoms with olefins produces olefin oxides and their isomeric aldehydes and ketones.[12] In the case of 1-butene, 1-butene oxide (0.53), butanal (0.43), and 2-butanone (0.04) are produced. The numbers in parentheses are the fractions of the total addition products observed in the gas phase at room temperature. In a previous paper,[4] we investigated the γ-ray-induced oxidation of several olefins in liquid carbon dioxide at -18 °C and found, in the case of 1-butene, that the fractions of the total addition products are 0.70 for 1-butene oxide, 0.25 for butanal, and 0.05 for 2-butanone. The difference between these fractions and those obtained in the gas-phase reaction may be attributed to the interaction between the intermediate biradical formed in the reaction of oxygen atoms with 1-butene and carbon dioxide.

When dinitrogen oxide was used in place of carbon dioxide, the formation of 1-butene oxide, butanal, and 2-butanone was again observed, as is shown in Fig. 2, and the *G*-values were found to be proportional to the electron fraction of dinitrogen oxide up to 0.8, suggesting that these products are formed in the reaction of oxygen atoms generated by the radiolysis of dinitrogen oxide.

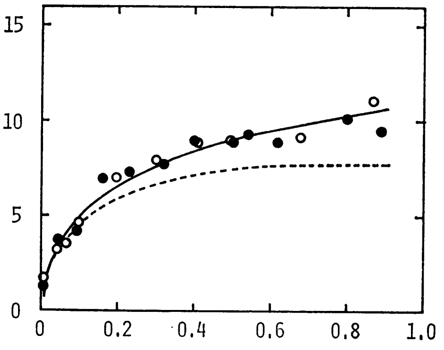

Fig. 1. The *G*-values of nitrogen from the two reaction systems; toluene (0.9)-1-butene(0.1)-N_2O (●) and benzene (0.6)-1,3,5-trimethylbenzene (0.4)-N_2O (○), as a function of the electron fraction ε of dinitrogen oxide.
The dotted line is the *G*-value of nitrogen produced by ionic process. Both solid and dotted lines are theoretical.

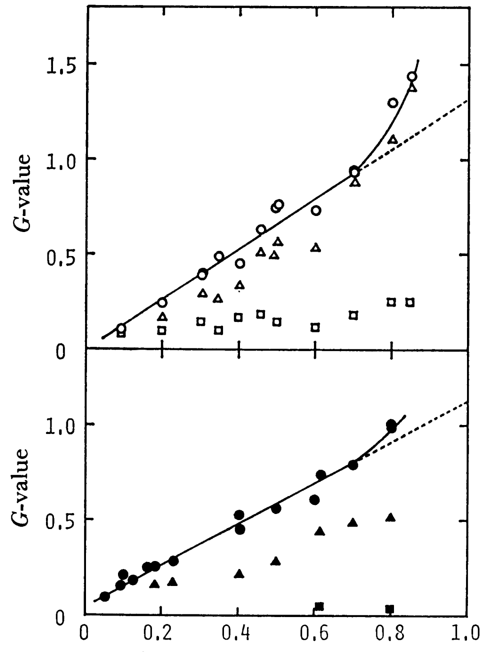

Fig. 2. The *G*-values of 1-butene oxide (○, ●), butanal (△, ▲), and 2-butanone (□, ■) as functions of the electron fraction ε of dinitrogen oxide.
Open symbols for the 1-butene-N_2O system and filled ones for the toluene (0.9)-1-butene (0.1)-N_2O system.

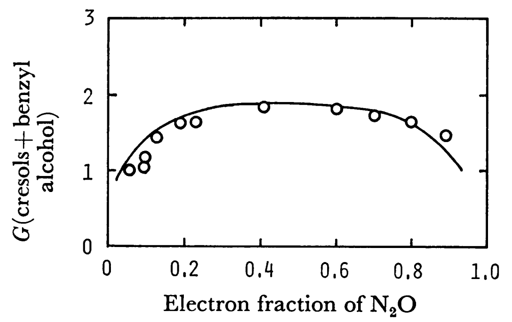

Fig. 3. The *G*-values of the sum of three kinds of cresols and benzyl alchol as a function of the electron fraction ε of dinitrogen oxide in the toluene (0.9)-1-butene (0.1)-N_2O system.
The solid line was calculated theoretically.

$$N_2O \rightsquigarrow N_2 + O \tag{1}$$

$$O + \text{1-Butene} \longrightarrow \text{1-Butene Oxide, Butanal, 2-Butanone} \tag{2}$$

The fractions of these products against the total addition products calculated from the slopes of the linear dependence of the *G*-values of these products on ε, however, are not the real fractions corresponding to Reaction 2, because a part of butanal and 2-butanone are believed to be formed by the reaction between 1-butene and the ionic species generated in this system. A similar observation has been made with regard to the formation of cyclohexanol in the γ-radiolysis of the mixture of cyclohexene and dinitrogen oxide.[1]

Above 0.8 of the electron fraction of dinitrogen oxide, another process for the formation of oxygen atoms has to be considered, for which we propose the following reactions:

$$N_2O \rightsquigarrow N_2O^+ + e^- \tag{3}$$

$$e^- + N_2O \longrightarrow N_2O^- \tag{4}$$

$$\begin{aligned} N_2O^+ + N_2O^- &\longrightarrow 2N_2 + 2O \\ &\longrightarrow N_2 + O + N_2O. \end{aligned} \tag{5}$$

In the presence of a hydrocarbon, a charge transfer will occur, since the ionization potential of any hydrocarbon is smaller than that of dinitrogen oxide:

$$N_2O^+ + A \longrightarrow N_2O + A^+. \tag{6}$$

Here, A stands for a hydrocarbon. This process suppresses the formation of oxygen atoms.

As Fig. 2 shows, the formation of 1-butene oxide was reduced in the presence of toluene. Since toluene is also reactive to oxygen atoms, the decrease in *G*(1-butene oxide) allows us to estimate the relative rate constant of the oxygen atoms with 1-butene (k_B) and toluene (k_T) as follows:

$$(G_0 - G)/G = k_T[\text{toluene}]/k_B[\text{1-butene}].$$

Here, G and G_0 are the *G*-values of 1-butene oxide from the reaction system in the presence and in the absence of toluene. The substitution of the data shown in Fig. 2 gives the following ratio:

$$k_T/k_B = (1.30-1.12)/1.12\times 1/9 = 0.02.$$

The rate constants of the gas-phase reactions of oxygen atoms with hydrocarbons have been measured by Atkinson and Cvetanović[13] and by Atkinson and Pitts.[14,15] Using their data, we can estimate the rate constant ratio at −18 °C to be 0.008. Since the experimental error in activation energy is reported to be 30%, the ratio obtained in the present experiment may be regarded as being in agreement with the gas-phase data.

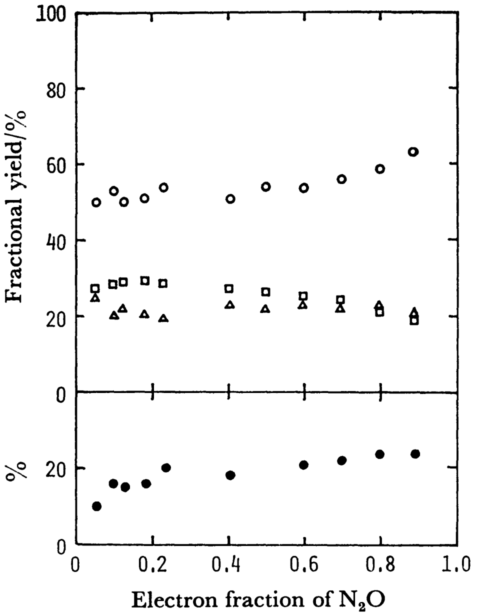

Fig. 4. The fractional yields of three kinds of cresols (○, ortho; □, meta; △, para) and benzyl alcohol (●) as functions of the electron fraction ε of dinitrogen oxide in the toluene (0.9)–1-butene (0.1)–N_2O system.

The Precursors of Cresols. Figure 4 shows the yield ratios of three kinds of cresols and benzyl alcohol from the toluene(0.9)–1-butene(0.1)–N_2O system as functions of the electron fraction of dinitrogen oxide. The numbers in parentheses are the mole fractions of the two hydrocarbons in the mixture. Since the ratio of ortho, meta, and para is dependent upon the electron fraction of dinitrogen oxide, we have to consider at least two precursors for the formation of these products. A comparison of Figs. 2 and 3 suggests that the precursors of cresols and benzyl alcohol are not oxygen atoms at low-electron fractions of dinitrogen oxide. Since dinitrogen oxide is a well-known electron scavenger, it may be natural to consider that the precursor is N_2O^- or O^- ions produced in the electron-scavenging reaction of dinitrogen oxide.

The reactions of N_2O^- ions in hydrocarbons, especially in cyclohexane, have been discussed by a number of researchers,[16–19] but they have not been established yet. In the present experiment, however, the similarity in the N_2O electron-fraction dependence of $G(N_2)$ and G(cresols+benzyl alcohol) at low values of ε strongly suggests that ionic species such as N_2O^- ions are the precursors of these products.

$$A \rightsquigarrow A^+ + e^- \qquad (7)$$

$$e^- + N_2O \longrightarrow N_2O^- \qquad (8)$$

$$N_2O^- + A \longrightarrow N_2 + AO^- \qquad (9)$$

$$AO^- + A^+ \longrightarrow P + A \qquad (10)$$

Here, A stands for an aromatic hydrocarbon, and P, for the addition product.

If this mechanism is operative, the ortho-meta-para ratio obtained in a low-electron fraction of dinitrogen oxide in the toluene–1-butene–N_2O system should correspond to the orientation of the addition of O^- to toluene. As Fig. 4 shows, the ratio at the lower limit of the electron fraction of dinitrogen oxide is 53: 27: 20.

In high-electron fractions, this ratio approaches 65: 15: 20 with the increase in ε. This ratio is close to that obtained in the gas-phase reaction of oxygen atoms with toluene (64: 17: 19).[20] In the previous section, we stated that oxygen-atom generation increases with the increase in ε above 0.8. Consequently, we may conclude that oxygen atoms become important precursors for cresols in high-electron fractions of dinitrogen oxide.

Below we will discuss a reaction mechanism which is applicable to all the range of ε; the kinetic treatment will be presented at that time.

Benzene–1,3,5-Trimethylbenzene–N_2O System. Figure 5 shows the G-values of phenol, 2,4,6-trimethylphenol, and 3,5-dimethylbenzyl alcohol as functions of ε from the mixture of benzene (0.6), 1,3,5-trimethylbenzene (0.4), and N_2O. The numbers in parentheses are the mole fractions of the two hydrocarbons in the mixture. It may be worthwhile to mention here that the electron-fraction dependence of G(phenol) is similar to that of G(3,5-dimethylbenzyl alcohol), but different from that of G(2,4,6-trimethylphenol).

According to Grovenstein and Mosher,[20] the forma-

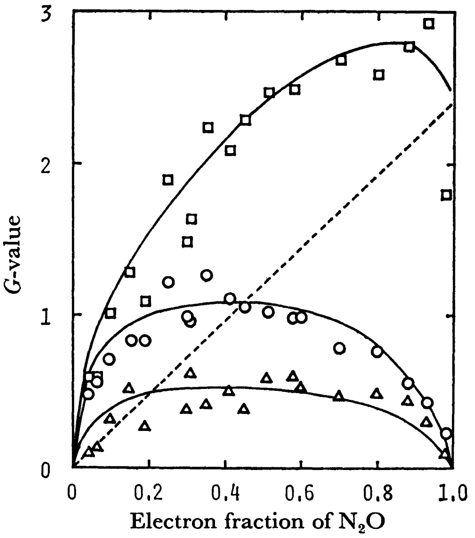

Fig. 5. The G-values of phenol (○), 2,4,6-trimethylphenol (□), and 3,5-dimethylbenzyl alcohol (△) as functions of the electron fraction ε of dinitrogen oxide in the benzene (0.6)–1,3,5-trimethylbenzene (0.4)–N_2O system.

Solid lines are theoretical. The dotted line is the G-value of 2,4,6-trimethylphenol formed in the reaction of oxygen atoms.

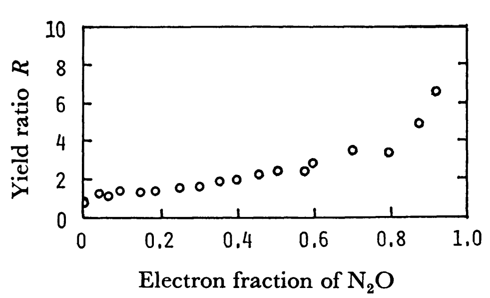

Fig. 6. The yield ratio R of [2,4,6-trimethylphenol]/[phenol] as a function of the electron fraction ε of dinitrogen oxide in the benzene (0.6)–1,3,5-trimethylbenzene (0.4)–N_2O system.

tion of phenols in the gas-phase reactions of oxygen atoms with aromatic hydrocarbons is faster for the more methyl-substituted ones. In the case of the competition between benzene and 1,3,5-trimethylbenzene, the reaction-rate ratio (R) for 2,4,6-trimethylphenol to phenol has been reported to be 77.5. The ratio obtained in the present experiment is plotted in Fig. 6 as a function of ε. As ε approaches unity, the ratio, R, seems to approach the value obtained by Grovenstein and Mosher, while at low values of ε, R is about unity.

In order to estimate the fractions of 2,4,6-trimethylphenol produced through two processes, one from the reaction of oxygen atoms and the other from the reaction of ionic species, we made a few experiments in which the mole fractions of benzene and 1,3,5-trimethylbenzene were changed in the presence of a constant electron fraction of dinitrogen oxide at 0.1. The results are shown in Fig. 7.

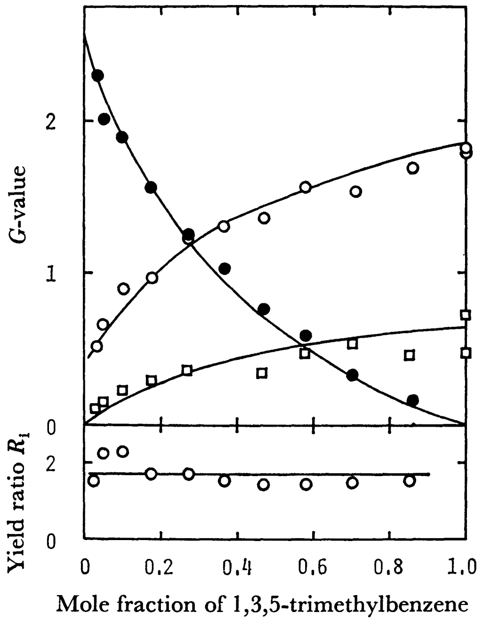

Fig. 7. The G-values of addition products from the benzene–1,3,5-trimethylbenzene system in the presence of dinitrogen oxide (ε=0.1) at 0°C and the yield ratio, R_I, as functions of the mole fraction of 1,3,5-trimethylbenzene.

●, Phenol; ○, 2,4,6-trimethylphenol; □, 3,5-dimethylbenzyl alcohol.

$$R_I = \frac{G_i(\text{2,4,6-trimethylphenol})}{G_i(\text{phenol})} \quad \frac{[\text{benzene}]}{[\text{1,3,5-trimethylbenzene}]}$$

It is known in the gas-phase reaction that the phenol formation in the reaction of oxygen atoms with benzene is only 6% of the consumption of oxygen atoms.[21] This percentage may not be very different in the liquid-phase reaction. Moreover, benzene is much less reactive to oxygen atoms than is 1,3,5-trimethylbenzene. The phenol observed in the present experiment, therefore, may be assumed to be produced only from the reaction of ionic species with benzene:

$$\text{benzene} + N_2O^- \longrightarrow \text{phenol} \qquad (11)$$

$$\text{1,3,5-trimethylbenzene} + N_2O^- \longrightarrow \text{2,4,6-trimethylphenol} \qquad (12)$$

$$\text{1,3,5-trimethylbenzene} + O \longrightarrow \text{2,4,6-trimethylphenol}. \qquad (13)$$

Since the formation-rate ratio of the 2,4,6-trimethylphenol produced by Reaction 12 to the phenol produced by Reaction 11 should be constant, this ratio can be calculated by using the data shown in Fig. 7 on the assumption that the extra amount of 2,4,6-trimethylphenol is produced by Reaction 13. The ratio thus estimated is 1.7. The plots for this estimation are also shown in Fig. 7.

Let us go back to the data shown in Fig. 5, where the mole-fraction ratio of benzene to 1,3,5-trimethylbenzene is 0.6: 0.4. Consequently, the G_i(2,4,6-trimethylphenol)/G_i(phenol) ratio in this experiment should be 1.1 ($=1.7\times0.4/0.6$). Here, G_i stands for the G-value of the product formed by the reaction of ionic species. Using this ratio, we can estimate the G-value of the 2,4,6-trimethylphenol produced by the reaction of oxygen atoms, on the assumption that the phenol observed is produced only from the reaction of ionic species. Figure 8 shows the G-values thus calculated as a function of the electron fraction of dinitrogen oxide. The G-values are obviously linearly dependent

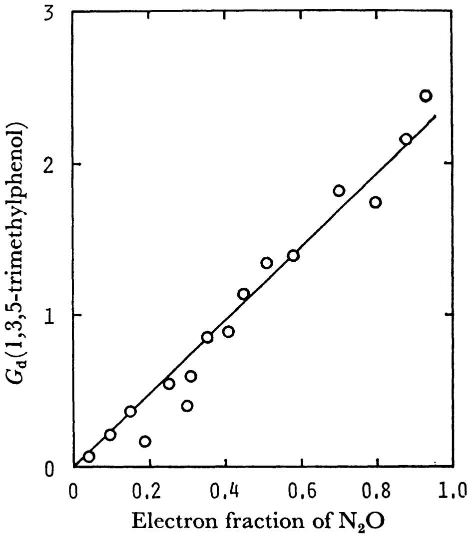

Fig. 8. The G-value of 2,4,6-trimethylphenol formed in the reaction of oxygen atoms produced by the direct radiolysis of dinitrogen oxide.

upon ε; this is consistent with the assumption made above that this part of the 2,4,6-trimethylphenol is produced by the reaction of oxygen atoms. The G-value of the 2,4,6-trimethylphenol produced by this process is calculated to be 2.4ε.

The Precursor of Benzyl-alcohol-type Products. So far two benzyl alcohol-type products have been found; one is benzyl alcohol from the toluene–N_2O system, and the other is 3,5-dimethylbenzyl alcohol from the benzene-1,3,5-trimethylbenzene–N_2O system. The dependence of G(benzyl alcohol) on the electron fraction of dinitrogen oxide was similar to that of G(cresols), although the absolute yield was very small when ε was close to unity. On the other hand, as Fig. 5 shows, the dependence of G(3,5-dimethylbenzyl alcohol) on ε was very similar to that of G(phenol).

According to Jones and Cvetanović,[22] no benzyl alcohol was formed in the gas-phase reaction of oxygen atoms with toluene. Consequently, we may conclude that both benzyl alcohol and 3,5-dimethylbenzyl alcohol are produced from the reaction with ionic species, although the mechanism cannot be specified in detail. In the following treatment, we tentatively assume that the mechanism of the formation of benzyl alcohols is similar to that of the isomeric phenols produced through the ionic process.

Kinetic Treatment. The neutralization reaction of geminate ion-pairs produced in the γ-irradiated system cannot be treated by a simple kinetic treatment in which the reaction rate is assumed to be always proportional to the reactant concentration in the solution. Consequently, several empirical equations have been proposed for the interpretation.[23–25] Among them, the so-called Schuler equation is the most famous.

In a previous paper,[26] we investigated the electron-scavenging process of bromobenzene in the γ-irradiated cyclohexane and 2,2,4-trimethylpentane, and concluded that the following Hummel empirical equation was better than Schuler's in explaining the wide range of concentrations of electron scavengers:

$$G(P) = G_{fi} + G_{gi}[1-\exp(-\sqrt{\alpha S})]. \tag{I}$$

Here, G(P) is the G-value of the electrons scavenged by a solute, with S as its concentration. G_{fi} and G_{gi} are the G-values of free and geminate electrons respectively, and α is an empirical constant proportional to the rate constant of the electron-scavenging reaction. The $\exp(-\sqrt{\alpha S})$ term on the right-hand side is the fraction which is not scavenged by the scavenger.

On the other hand, if the time distribution of the geminate electrons is denoted by $f_e(t)$, the fraction which is not scavenged by the scavenger may be written as follows:

$$\int_0^\infty f_e(t)\exp(-kSt)\mathrm{d}t = \exp(-\sqrt{\alpha S}). \tag{II}$$

Here, k is the rate constant of the electron scavenging and is related to α by $\alpha = k/\lambda$. λ is a constant depending on the solvent.[27] Using Eq. II, we can derive the concentration dependence of the electron-scavenging reaction without the knowledge of the time distribution of the geminate electrons.

In order to develop a theoretical treatment, we will now consider the phenol formation through the ionic process in the γ-radiolysis of a mixture of benzene and dinitrogen oxide. We propose the following reaction mechanism:[6]

$$C_6H_6 \rightsquigarrow C_6H_6^+ + e^- \tag{14}$$

$$N_2O \rightsquigarrow N_2O^+ + e^- \tag{15}$$

$$N_2O^+ + C_6H_6 \longrightarrow N_2O + C_6H_6^+ \tag{16}$$

$$e^- + N_2O \xrightarrow{k_e} N_2O^- \tag{17}$$

$$N_2O^- + N_2O \xrightarrow{k_s} N_2 + N_2O_2^- \tag{18}$$

$$N_2O^- + C_6H_6 \xrightarrow{k_a} N_2 + C_6H_6O^- \tag{19}$$

$$C_6H_6O^- + N_2O \xrightarrow{k_b} N_2 + C_6H_6O_2^- \tag{20}$$

$$C_6H_6^+ + e^- \longrightarrow Q \tag{21}$$

$$C_6H_6^+ + N_2O^- \xrightarrow{a} N_2 + P \tag{22}$$

$$C_6H_6^+ + N_2O_2^- \longrightarrow N_2 + Q \tag{23}$$

$$C_6H_6^+ + C_6H_6O^- \xrightarrow{b} P + C_6H_6 \tag{24}$$

$$C_6H_6^+ + C_6H_6O_2^- \xrightarrow{c} P + Q. \tag{25}$$

Here, Q stands for some products other than phenol, and P, for phenol. k_e, k_s, k_a, and k_b are the rate constants for the corresponding reactions. The a, b, and c shown in Reactions 22, 24, and 25 are the fractions of the phenol formation in these reactions. Reaction 20 was included to explain the large G-value of nitrogen. Reaction 22 is regarded as being similar to the reaction of oxygen atoms with benzene; therefore, the parameter, a, is taken to be equal to the conversion ratio of the phenol formation to the consumption of oxygen atoms. The phenol formation was not assumed in Reaction 23, since this reaction may be similar to the reaction of excited O_2 molecules with benzene. The reaction of $N_2O_2^-$ ions with benzene was not included, since the reactivity of $N_2O_2^-$ ions may be similar to that of superoxide ions. Superoxide ions are known not to be reactive to benzene.[28]

First, let us consider the lifetimes of negative species. The lifetime of a geminate electron produced in the system is denoted by t. If this electron is scavenged by N_2O at the time t', the lifetime of the negative charge will be prolonged, since the mobility of negative ions is much smaller than that of electrons. The lifetime of the N_2O^- ions thus produced may be expressed by $(t-t')r_D$, where $r_D = (\mu_e + \mu_+)/(\mu_- + \mu_+)$, and where μ_e, μ_+, and μ_- are the mobilities of electrons, $C_6H_6^+$ ions, and N_2O^- ions respectively. According to Reactions 18 and 19, N_2O^- ions react with N_2O or C_6H_6. If either of these reactions occurs at t'' after the formation of N_2O^- ions, the lifetime of the newly formed $N_2O_2^-$ or $C_6H_6O^-$ ions may be expressed by $[(t-t')r_D - t'']$. Here, we assumed that all of the negative ions have the same mobility, μ_-.

Since the probability that electrons are not scavenged by N_2O by the time t' is expressed by $\exp(-k_e[N_2O]t')$, and, similarly, the probability that N_2O^- does not react with N_2O or C_6H_6 by the time t'' after its generation is expressed by $\exp(-k_s[N_2O]t'' - k_a[C_6H_6]t'')$, the fraction of the nitrogen formation by Reaction 18 may be expressed as follows:

$$F_{18}(\mathrm{N_2}) = \int_0^\infty f_{\mathrm{e}}(t)\mathrm{d}t \int_0^t k_{\mathrm{e}}[\mathrm{N_2O}] \exp(-k_{\mathrm{e}}[\mathrm{N_2O}]t')\mathrm{d}t'$$
$$\times \int_0^{(t-t')r_{\mathrm{D}}} k_{\mathrm{s}}[\mathrm{N_2O}] \exp(-k_{\mathrm{s}}[\mathrm{N_2O}]t'' - k_{\mathrm{a}}[\mathrm{C_6H_6}]t'')\mathrm{d}t''. \tag{III}$$

After the integrations are carried out, the use of Eq. II gives the following equation:

$$F_{18}(\mathrm{N_2}) = \frac{\beta S}{\beta S+\delta}\left[1-\exp(-\sqrt{\alpha S}) - \frac{\alpha S}{\alpha S-(\beta S+\delta)}\right.$$
$$\left.\times\{\exp(-\sqrt{\beta S+\delta})-\exp(-\sqrt{\alpha S})\}\right]. \tag{IV}$$

Here, $\alpha = k_{\mathrm{e}}/\lambda$, $\beta = (k_{\mathrm{s}}/\lambda)r_{\mathrm{D}}$, and $\delta = (k_{\mathrm{a}}[\mathrm{C_6H_6}]/\lambda)r_{\mathrm{D}}$. In similar manners, all of the fractions of the nitrogen formation through ionic processes can be derived. As for free electrons, we can use a usual kinetic treatment. Since the concentration of dinitrogen oxide used in the present experiment is not very small, all of the free electrons are assumed to be scavenged by $\mathrm{N_2O}$. The fraction of the nitrogen formation initiated by free electrons may be written as follows:

$$F_{\mathrm{fi}}(\mathrm{N_2}) = \left(1+\frac{\beta S}{\beta S+\delta}+\frac{\delta}{\beta S+\delta}\frac{R_{20}}{R_{20}+R_{24}}\right). \tag{V}$$

Here, R_{20} and R_{24} are the reaction rates of the corresponding reactions. For simplicity, we assume the following expression for the ratio of R_{20}/R_{24}:[29]

$$R_{20}/R_{24} = [\mathrm{N_2O}]/0.1 \tag{VI}$$

Ultimately we can obtain the following expression for the G-value of nitrogen produced through ionic processes:

$$G_{\mathrm{i}}(\mathrm{N_2}) = G_{\mathrm{fi}}P_1 + G_{\mathrm{gi}}[1-\exp(-\sqrt{\alpha S})]P_2 \tag{VII}$$

$$P_1 = F_{\mathrm{fi}}(\mathrm{N_2}) \tag{VIII}$$

$$P_2 = 2 - \frac{\alpha S}{\alpha S-(\beta S+\delta)}\left\{1-\frac{1-\exp(-\sqrt{\beta S+\delta})}{1-\exp(-\sqrt{\alpha S})}\right\}$$
$$-\frac{\delta}{\beta S+\delta-\gamma S}\left(\frac{\alpha}{\alpha-\gamma}\left\{1-\frac{1-\exp(-\sqrt{\gamma S})}{1-\exp(-\sqrt{\alpha S})}\right\}\right.$$
$$\left.-\frac{\alpha S}{\alpha S-(\beta S+\delta)}\left\{1-\frac{1-\exp(-\sqrt{\beta S+\delta})}{1-\exp(-\sqrt{\alpha S})}\right\}\right]. \tag{IX}$$

Here, $\gamma = (k_{\mathrm{b}}/\lambda)r_{\mathrm{D}}$. When this equation is applied to a very low concentration of a scavenger, the term for G_{fi} has to be accurately formulated.[30] In the present calculation, the contribution of G_{fi} is very small, since the G-values of the free electrons in aromatic hydrocarbons are known to be small:[31,32] for example, 0.06 for benzene, 0.05 for toluene, 0.07 for *p*-xylene, and 0.09 for 1,3,5-trimethylbenzene.

The expression for the phenol formation through an ionic process can similarly be derived as follows:

$$G_{\mathrm{i}}(\mathrm{P}) = G_{\mathrm{fi}}Q_1 + G_{\mathrm{gi}}[1-\exp(-\sqrt{\alpha S})][aQ_2+cQ_3$$
$$+(b-c)Q_4] \tag{X}$$

$$Q_1 = \left[b+(c-b)\frac{S}{S+0.1}\right]\frac{\delta}{\beta S+\delta} \tag{XI}$$

$$Q_2 = \frac{\alpha S}{\alpha S-(\alpha S+\delta)}\left[1-\frac{1-\exp(-\sqrt{\beta S+\delta})}{1-\exp(-\sqrt{\alpha S})}\right] \tag{XII}$$

$$Q_3 = \frac{\delta}{\beta S+\delta}(1-Q_2) \tag{XIII}$$

$$Q_4 = \frac{\alpha}{\alpha-\gamma}\left[1-\frac{1-\exp(-\sqrt{\gamma S})}{1-\exp(-\sqrt{\alpha S})}\right] - Q_2. \tag{XIV}$$

Here, the phenol formation initiated by free electrons is assumed to result only from Reactions 24 and 25.

In order to determine the parameters appearing in the above expressions, we used two sets of experimental results; one consisted of the G-values of nitrogen and phenol obtained at low concentrations of dinitrogen oxide at room temperature, since benzene containing a small amount of dinitrogen oxide is crystallized at around 0 °C, while the other consisted of G(phenol)'s from a benzene–$\mathrm{N_2O}$ system at 0 °C.

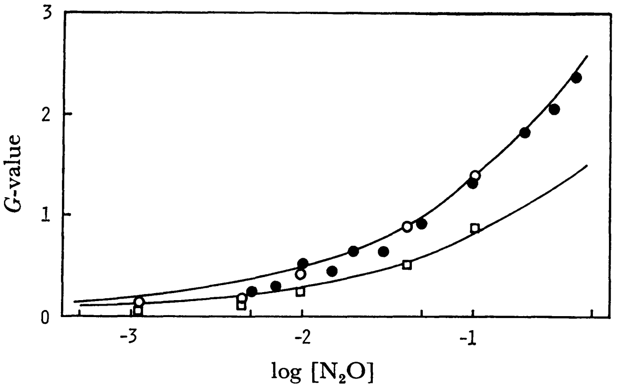

Fig. 9. The G-values of nitrogen (○, ●) and phenol (□) from the benzene–$\mathrm{N_2O}$ system at room temperature.
Solid lines are theoretical. Open symbols for the present work, and filled ones for the result of Hentz and Sherman.

Figure 9 shows $G(\mathrm{N_2})$ and G(phenol) at low concentrations of dinitrogen oxide, together with the results obtained by Hentz and Sherman.[33] The solid lines are the results of the calculation using Eqs. VII and X. The parameters used are $G_{\mathrm{fi}}=0.06$, $G_{\mathrm{gi}}=3.8$, $\alpha=0.5$ $\mathrm{dm^3\,mol^{-1}}$, $\beta=\gamma=1.0$ $\mathrm{dm^3\,mol^{-1}}$, $\delta=9.0[\mathrm{C_6H_6}]$, $a=0.0$, and $b=c=1.0$. Here, we assumed $a=0.0$, since the fraction of the phenol formation against the consumption of oxygen atoms is known to be very small (6%) in the gas-phase reaction of oxygen atoms with benzene.

Figure 10 shows the G(phenol)'s as a function of ε from the benzene–$\mathrm{N_2O}$ system obtained at 0 °C. A solid line was calculated by using the same parameter as above. The deviation of the experimental plots at high-electron fractions above 0.9 might be due to the

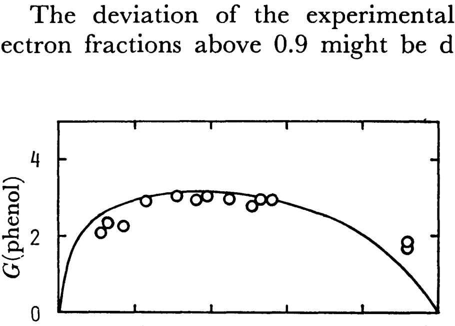

Fig. 10. The G-value of phenol from the benzene–$\mathrm{N_2O}$ system at 0°C. A solid line is theoretical.

phenol formation from the reaction of oxygen atoms with benzene. This point will be discussed later.

Now, let us go back to the data of $G(N_2)$ shown in Fig. 1. There are two origins of nitrogen in this reaction system, one is the direct radiolysis of dinitrogen oxide, $G_d(N_2)$, and the other, from the ionic process, $G_i(N_2)$:

$$G(N_2) = G_d(N_2) + G_i(N_2). \qquad \text{(XV)}$$

$G_d(N_2)$ should be proportional to ε up to 0.8. The dotted line shown in Fig. 1 is $G_i(N_2)$ calculated by using Eq. VII. A solid line was drawn by adding 3.3ε to $G_i(N_2)$. Because of the scattering of the $G(N_2)$ data, only a wide range of the value, $G_d(N_2)/\varepsilon = 3.0$—$4.0$, can be estimated from Fig. 1. The value of 3.3 was estimated as follows. In the 1-butene–N_2O system, we observed that $G(\text{1-butene oxide}) = 1.4\varepsilon$. On the other hand, according to Cvetanović,[12] the yield of 1-butene oxide upon the consumption of oxygen atoms is about 0.42 in the gas-phase reaction. If we take this value for the present experiment, the G-value of the oxygen atoms produced by the direct radiolysis of dinitrogen oxide should be 3.3 (=1.4/0.42).

If we take this value, 3.3, as the G-value of the oxygen atoms from the direct radiolysis of dinitrogen oxide, the conversion yield, $a = G_d(\text{2,4,6-trimethylphenol})/G_d(\text{oxygen atoms})$, in the benzene–1,3,5-trimethylbenzene–N_2O system is calculated to be 0.71 (=2.4/3.3).

It may be worthwhile here to make some comments on the parameters we have used above. When Hentz and Sherman analyzed $G(N_2)$,[33] they used Schuler's empirical equation, which is exactly the same as Hummel's equation at the lower limit of the scavenger concentration. The α parameter they obtained was about 0.7 $\text{dm}^3\,\text{mol}^{-1}$. For the β parameter, they could not determine the exact value because of the scattering of data, but they suggested that it is larger than α. We have no knowledge to use for the estimation of the value of γ; however, Reactions 18 and 20 are similar in the mechanism of the oxygen-atom transfer, so that $\beta=\gamma$ may not be an absurd approximation. Reaction 19 is practically the addition reaction of O^- to benzene; therefore, $\delta/[C_6H_6]$ must be much larger than β and γ. We took 9.0 for this ratio.

The Competition of Aromatic Hydrocarbons for the Formation of the Corresponding Phenols by the Ionic Process. In order to investigate the competition of aromatic hydrocarbons for the formation of the corresponding phenols, the following three mixtures were γ-irradiated at various mixing ratios under a constant electron fraction of dinitrogen oxide ($\varepsilon=0.1$); benzene–toluene, benzene–*p*-xylene, and benzene–1,3,5-trimethylbenzene. The results for the last mixture have already been shown in Fig. 7.

When two aromatic hydrocarbons, A and B, are used in place of benzene in the reaction mechanism stated above, competition between A and B occurs in Reactions 19 and 20:

$$N_2O^- + A \xrightarrow{k_A} N_2 + AO^- \qquad \text{(19A)}$$

$$N_2O^- + B \xrightarrow{k_B} N_2 + BO^- \qquad \text{(19B)}$$

$$AO^- + N_2O \longrightarrow N_2 + AO_2^- \qquad \text{(20A)}$$

$$BO^- + N_2O \longrightarrow N_2 + BO_2^-. \qquad \text{(20B)}$$

The kinetic treatment including these reactions is somewhat complicated; however, when the electron fraction of dinitrogen oxide is not very large, the following approximate expression can be used:

$$G_i(P_A) = \frac{k_A[A]}{k_A[A]+k_B[B]}[b_A G_{fi} + c_A G_{gi}(1-e^{-\sqrt{aS}})] \qquad \text{(XVI)}$$

$$G_i(P_B) = \frac{k_B[B]}{k_A[A]+k_B[B]}[b_B G_{fi} + c_B G_{gi}(1-e^{-\sqrt{aS}})]. \qquad \text{(XVII)}$$

Here, the subscripts A and B correspond to the two hydrocarbons, A and B. Since G_{fi} is much smaller than G_{gi}, the contribution of the first term in brackets on the right-hand side is very small compared with the second one. The errors introduced in the estimation of k_A/k_B by using these approximate expressions were calculated numerically and estimated to be within 10%.

Since the gas-chromatographic analysis of products was not very reproducible, as will be shown below, we used the following procedure for the determination of the relative rate constants, k_A/k_B. This procedure has already been used in a previous paper,[4] where the relative rate constants of oxygen atoms with several olefins were determined.

In the case of benzene, the only addition product observed is phenol, but in the case of toluene we observed three kinds of cresols and benzyl alcohol, so that the process for the formation of addition products has to be divided:

$$N_2O^- + A \xrightarrow{m} P_{Am}$$

$$\xrightarrow{1-m} P_{A(1-m)}.$$

Here, m denotes the fraction of the P_{Am} product against the total addition products from the A hydrocarbon. Now, let us introduce a weighted mole fraction, x:

$$x = \frac{f[B]}{[A]+f[B]}, \qquad \text{(XVIII)}$$

where f is the factor to be estimated. If the f factor is equal to the k_B/k_A ratio, the plots of $G(P_{Am})$ against x will give a straight line:

$$G(P_{Am}) = mG_A(1-x). \qquad \text{(XIX)}$$

Here,

$$G_A = b_A G_{fi} + c_A G_{gi}(1-e^{-\sqrt{aS}}). \qquad \text{(XX)}$$

A similar linearity can be obtained for the products of the reaction with the B hydrocarbon:

$$G(P_{Bn}) = nG_B x. \qquad \text{(XXI)}$$

Here,

$$G_B = b_B G_{fi} + c_B G_{gi}(1-e^{-\sqrt{aS}}), \qquad \text{(XXII)}$$

and n is the fraction of the P_{Bn} product. Such plots are made by varying the f factor until good linearities are obtained for all products.

Figures 11, 12, and 13 show the final plots thus obtained for the reaction systems of benzene–toluene, benzene–*p*-xylene, and benzene–1,3,5-trimethylbenzene respectively. Figure 13 clearly shows the intercept at [1,3,5-trimethylbenzene]=0 for the plots of 2,4,6-trimethylphenol. This is due to the reaction of the

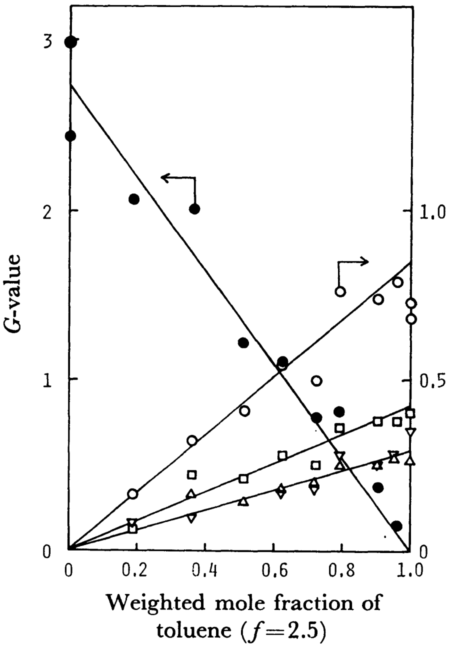

Fig. 11. The G-values of addition products from the mixture of benzene and toluene in the presence of dinitrogen oxide (ε=0.1) at 0°C as functions of the weighted mole fraction of toluene.
The value of f is taken as 2.5. ●, Phenol; ○, *o*-cresol; □, *m*-cresol; △, *p*-cresol; ▽, benzyl alcohol.

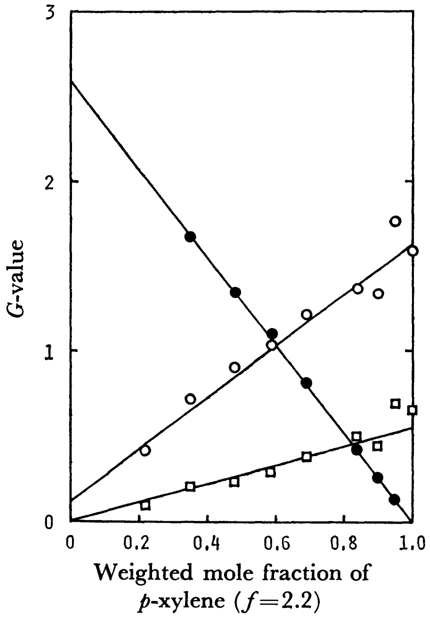

Fig. 12. The G-values of addition products from the mixture of benzene and p-xylene in the presence of dinitrogen oxide (ε=0.1) at room temperature as functions of the weighted mole fraction of p-xylene.
The value of f is taken as 2.2. ●, Phenol; ○, 2,5-dimethylphenol; □, p-methylbenzyl alcohol.

oxygen atoms produced in the direct radiolysis of N_2O. The relative rate constants of Reaction 19 thus obtained are summarized in Table 1.

Now, let us go back to Eq. X. Most of the parameters in this equation for the aromatic hydrocarbons are known except for a, b, and c. Since ε is 0.1, we can neglect the phenol formation from the reaction of oxygen atoms with benzene, *i.e.*, a=0.0 in the case of the benzene system. Similarly, we assume here a=0.0 for the toluene system as well, since the ratio of the cresol formation to the consumption of oxygen atoms is known to be small (15%) in a gas-phase reaction.[22] As for 1,3,5-trimethylbenzene, we have already obtained a=0.71. For p-xylene, we tentatively assume a=0.4. As will be shown below, this value is consistent with the experimental results.

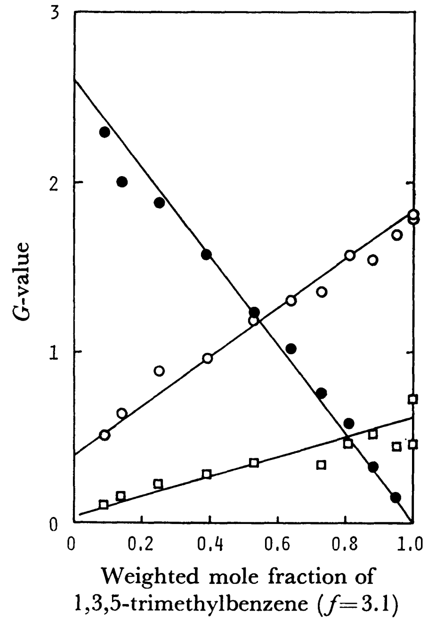

Fig. 13. The G-values of addition products from the mixture of benzene and 1,3,5-trimethylbenzene in the presence of dinitrogen oxide (ε=0.1) at 0°C as functions of the weighted mole fraction of 1,3,5-trimethylbenzene.
The value of f is taken as 3.1. ●, Phenol; ○, 2,4,6-trimethylphenol; □, 3,5-dimethylbenzyl alcohol.

TABLE 1. THE RELATIVE RATE CONSTANTS OF REACTIONS OF OXYGEN ATOMS AND N_2O^- IONS WITH SEVERAL HYDROCARBONS IN THE LIQUID PHASE

Reactions	Relative rate constants
O+benzene	1.0
O+toluene	2.0
O+1-butene	100
N_2O^-+benzene	1.0
N_2O^-+toluene	2.5
N_2O^-+p-xylene	2.2
N_2O^-+1,3,5-trimethylbenzene	3.1
N_2O^-+1-butene	6.25

The total G-value of a specified product, P_α, may now be expressed as follows:

$$G(P_\alpha) = G_d(P_\alpha) + G_i(P_\alpha) \qquad \text{(XXIII)}$$

$$G_d(P_\alpha) = laG_d(\text{oxygen atoms}) \qquad \text{(XXIV)}$$

$$G_i(P_\alpha) = G_{fi}Q_1la + G_{gi}(1-e^{-\sqrt{aS}}) \times [laQ_2+mcQ_3+m(b-c)Q_4]. \qquad \text{(XXV)}$$

Table 2. The parameters estimated for the theoretical calculation

$\alpha=0.5$ dm^3 mol^{-1}, $\beta=\gamma=1.0$ dm^3 mol^{-1}, $\delta/[C_6H_6]=9.0$

Reactant	a	$b=c$	Product	l	m
Benzene	0.17	1.0	Phenol	1.0	1.0
Toluene	0.36	0.74	*o*-Cresol	0.64	0.45
			m-Cresol	0.14	0.23
			p-Cresol	0.19	0.16
			Benzyl alcohol	0	0.16
			Phenol	0.03	0
p-Xylene	0.40	0.84	2,5-Dimethylphenol	1.0	0.75
			p-Methylbenzyl alcohol	0	0.25
1,3,5-Trimethylbenzene	0.71	0.81	2,4,6-Trimethylphenol	1.0	0.69
			3,5-Dimethylbenzyl alcohol	0	0.31

a: The fraction of the total addition products to the consumption of oxygen atoms; b: the fraction of the addition products to the consumption of N_2O^- ions; l: fractional yields of the addition products formed in the reaction of oxygen atoms; m: fractional yields of the addition products formed in the reaction of N_2O^- ions, followed by neutralization.

The expressions for Q_1, Q_2, Q_3, and Q_4 have already been shown in Eqs. XI, XII, XIII, and XIV respectively. l is the fraction of a specified product, P_α, against the total addition products formed in the reaction of oxygen atoms.

Table 2 summarizes all of the parameters used. These parameters can reproduce all the data shown in Figs. 11, 12, and 13 by the use of Eq. XXIII. As an example, the mole fraction dependence of the G-values of phenol, 2,5-dimethylphenol, and *p*-methylbenzyl alcohol is shown in Fig. 14. The dotted line shows the G-value of the 2,5-dimethylphenol produced through the ionic process (Eq. X).

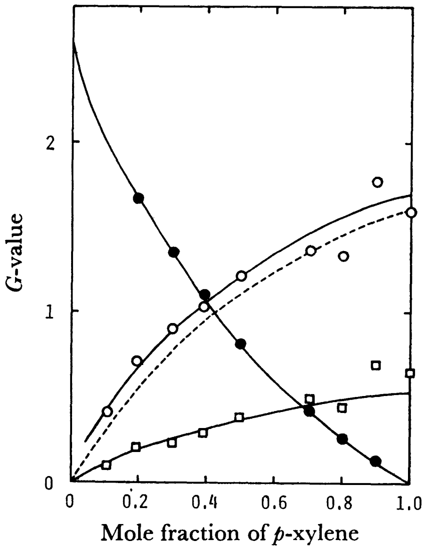

Fig. 14. The G-values of addition products from the benzene-*p*-xylene system in the presence of dinitrogen oxide ($\varepsilon=0.1$).

○, 2,5-Dimethylphenol; □, *p*-methylbenzyl alcohol; ●, phenol. Solid lines are theoretical. The dotted line is the G-value of 2,5-dimethylphenol produced through ionic process.

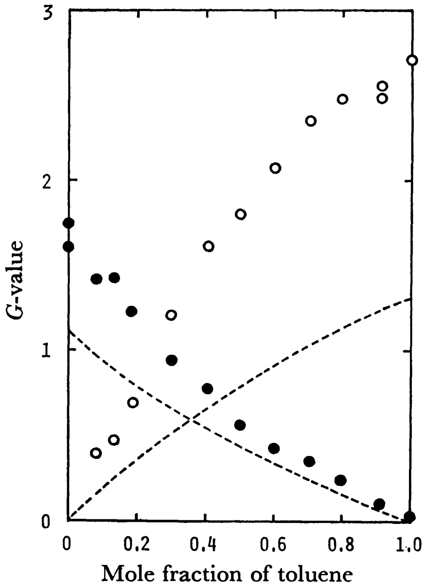

Fig. 15. The G-values of addition products from the benzene–toluene–N_2O system ($\varepsilon=0.92$).

○, The sum of cresols and benzyl alcohol; ●, phenol. Dotted lines are the G-values of each product formed through ionic process.

The Phenol and Cresol Formations in the Reactions of Oxygen Atoms with Benzene and Toluene. In the above calculation, we assumed $a=0.0$ in the cases of benzene and toluene. In order to estimate the real values, we have investigated the phenol and cresol formations at a high electron fraction of dinitrogen oxide ($\varepsilon=0.92$), where the oxygen atoms produced from the direct radiolysis of dinitrogen oxide are important as the source of phenol formation. The results are shown in Fig. 15. The dotted lines are the G-values of the products formed through the ionic process, which have been calculated by using Eq. X.

The difference in G-value between experiment and calculation is plotted in Fig. 16 by using the "weighted-mole-fraction" procedure. From this figure, we can estimate $a=0.17$ $(=0.52/(3.3\times0.92))$ for benzene and 0.36 $(=1.1/(3.3\times0.92))$ for toluene, and also

$$k(O+\text{toluene})/k(O+\text{benzene}) = 2.0.$$

Here, k is the rate constant of each reaction. Moreover, we can observe the intercept of G(phenol) at [benzene] =

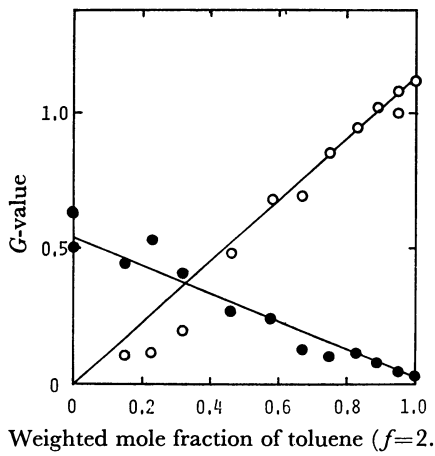

Fig. 16. The G-values of addition products formed in the reaction of oxygen atoms in the benzene–toluene–N_2O system ($\varepsilon=0.92$) as functions of the weighted mole fraction of toluene. ○, The sum of cresols; ●, phenol.

0, which suggests that a small amount of phenol is formed in the reaction of oxygen atoms with toluene. The G-value is calculated to be 0.03. This type of reaction has already been discussed by Sakurai *et al.*[8]

The Calculations of G*(phenol)'s from the Toluene–1-Butene–N_2O System and of the* G*-values of the Addition Products from the Benzene–1,3,5-Trimethylbenzene–N_2O System.* We now have all of the parameters necessary to calculate the G-values of the addition products shown in Figs. 3 and 5 by using Eq. XXIII, except for the rate-constant ratio, $k(N_2O^- + \text{1-butene})/k(N_2O^- + \text{toluene})$. For this ratio, we assumed 2.5 so as to explain the experimental data. The calculated results are shown in Figs. 3 and 5 as solid lines: the figures suggest that all the data are now explainable by the reaction mechanism proposed.

Although all the data shown in the present paper can be explained by the proposed reaction mechanism, this does not necessarily mean that such reactions as Reactions 19 and 20 are real reactions occurring in the system for the formation of the corresponding phenols. There might be another interpretation. In order to establish these reactions, we have to observe AO^- and AO_2^- ions directly, or, we have to investigate similar reactions with other aromatic compounds containing different substituents.

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30) The accurate expressions for G_{fi} (N_2) and G_{fi} (phenol) can be derived as follows:

$$G_{\mathrm{fi}}(N_2) = \frac{1}{\sqrt{k_{\mathrm{n}}DW}}\left\{2k_{\mathrm{s}}[N_2O]+k_{\mathrm{a}}[C_6H_6] + \frac{k_{\mathrm{a}}k_{\mathrm{b}}[N_2O][C_6H_6]}{k_{\mathrm{b}}[N_2O]+\sqrt{k_{\mathrm{n}}D/W}} + \sqrt{k_{\mathrm{n}}D/W}\right\} \left\{1+\frac{k_{\mathrm{s}}[N_2O]}{\sqrt{k_{\mathrm{n}}D/W}}+\frac{k_{\mathrm{a}}[C_6H_6]}{k_{\mathrm{b}}[N_2O]+\sqrt{k_{\mathrm{n}}D/W}} \times\left(1+\frac{k_{\mathrm{b}}[N_2O]}{\sqrt{k_{\mathrm{n}}D/W}}\right)\right\}^{-1}$$

$$G_{\mathrm{fi}}(P) = \frac{1}{W}\left\{a+\frac{k_{\mathrm{a}}[C_6H_6]}{k_{\mathrm{b}}[N_2O]+\sqrt{k_{\mathrm{n}}D/W}}\left(b+\frac{ck_{\mathrm{b}}[N_2O]}{\sqrt{k_{\mathrm{n}}D/W}}\right)\right\} \left\{1+\frac{k_{\mathrm{s}}[N_2O]}{\sqrt{k_{\mathrm{n}}D/W}}+\frac{k_{\mathrm{a}}[C_6H_6]}{k_{\mathrm{b}}[N_2O]+\sqrt{k_{\mathrm{n}}D/W}} \times\left(1+\frac{k_{\mathrm{b}}[N_2O]}{\sqrt{k_{\mathrm{n}}D/W}}\right)\right\}^{-1}.$$

Here, k_{n} stands for the rate constant of the neutralization reaction between $C_6H_6^+$ ions and negative ions; *i.e.*, we assumed here $k_{\mathrm{n}}=k_{22}=k_{23}=k_{24}=k_{25}$. D is the dose rate, and $W=100/G_{\mathrm{fi}}$; *cf.* K. Okazaki, R. Yugeta, and S. Sato, *Bull. Chem. Soc. Jpn.*, **46**, 2066 (1973).

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