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Nitrous Oxide as an Electron Scavenger in the Radiolysis of Hydrocarbons

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Nitrous oxide has been used as an electron scavenger in the radiolysis of hydrocarbons: cyclohexane, cyclohexene, benzene, and their mixtures. Considering that the energy for the formation of an ion pair is about 25 eV. in hydrocarbons, 0.4 mol.l^{-1} of nitrous oxide is not enough to capture all the electrons ejected from irradiated hydrocarbons. In the case of cyclohexane, 70% of the ejected electrons seem to be captured by 0.4 mol.l^{-1} of nitrous oxide. In the case of benzene, $G(N_2)$ is about a half of that for cyclohexane. This has been explained tentatively in terms of the ability of benzene to capture electrons. The $G(H_2)$'s in the cases of cyclohexene and benzene have not shown any noticeable dependence on the concentration of nitrous oxide. This shows that hydrogen does not result from the neutralization in these systems. In order to clarify them, the primary processes in the radiolysis of cyclohexane have been further considered using the data previously obtained.

In an attempt to investigate the charge separation in the radiolysis of liquid hydrocarbons, various electron scavengers, such as iodine, methyl iodide and tetrachloromethane, have been used as solutes.[1,2] However, these compounds are known to be reactive to the free radicals as well as to the electrons produced in the radiolysis, so they are not quite suitable for discriminating the reactions of free radicals and charged species, both of which are believed to participate in the radiolysis of hydrocarbons.

Recently it has become clear that nitrous oxide is highly reactive to electrons, but not to free radicals.[3] The compound has been used as an additive in the radiolysis of water[4,5] and its reaction with hydrated electrons has been interpreted in terms of the following dissociative mechanism:

$$e_{aq} + N_2O \rightarrow N_2 + O^-$$

In the radiolysis of hydrocarbons, it is possible that nitrous oxide are capable of capturing the electrons ejected from irradiated hydrocarbons if its concentration is high enough. In fact, Scholes and Simic suggested in a preliminary report that such a reaction occurs in the radiolysis of cyclohexane.[6]

The present paper will report the results of an independently-undertaken study of the applicability of this technique to the radiolysis of cyclohexane, cyclohexene, and benzene, and mixtures of these hydrocarbons.

Experimental

Guaranteed-grade cyclohexane, cyclohexene and benzene, supplied by the Tooa-gosei Co., have been purified by the conventional method described elsewhere.[7] The final step in the purification was to pass the liquids separately through 1-m. silica gel columns. Impurities of less than 0.1% were detected in the purified cyclohexene by gas chromatography; such small impurities are believed to have no appreciable effect on the radiolysis studied. In the case of cyclohexane, special precaution was taken to eliminate olefin contamination.[7] Nitrous oxide supplied by the Takachiho-shoji Co. was used as supplied; no impurities were detected by gas chromatography.

Samples consisting of 5 ml. of each liquid were irradiated with ^{60}Co-γ rays at room temperature, at a does rate of 1.60×10^{17} eV. ml^{-1} min^{-1}. In estimating the dose, $G(Fe^{3+}) = 15.6$ was used in the Fricke dosimetry.

The products not condensable at the temperature of liquid nitrogen were measured by a Toepler pump attached to a gas burette and a cuprous oxide furnace kept at 240°C. In this furnace, hydrogen is combusted into water, which is then trapped at the temperature of liquid nitrogen. In the cyclohexane radiolysis, a fair amount of water was detected as a product in some cases, although the amounts measured by gas chromatography were not quantitatively reliable.

Since the solubilities of nitrous oxide in cyclohexane and cyclohexene were not known, they were determined at room temperature using the technique reported by Loprest.[8] The Ostwald absorption coefficients obtained are shown in Table I. The value obtained for

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[1] L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

[2] J. A. Stone and P. J. Dyne, *Can. J. Chem.*, **42**, 669 (1964).

[3] G. Czapski and J. Jortner, *Nature*, **188**, 50 (1960).

[4] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, **A267**, 443 (1962).

[5] G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1731 (1964).

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

[7] S. Sato and S. Shida, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 555 (1960).

[8] F. J. Loprest, *J. Phys. Chem.*, **61**, 1128 (1957).

benzene is in good agreement with the value 3.668 at 20°C listed in the International Critical Tables.

Table I. Ostwald absorption coefficients of nitrous oxide (22.9°C)

Solvent	Benzene	Cyclohexane	Cyclohexene
Coefficient	3.45	2.62	3.10

Results

Figure 1 shows the dose dependence of products in the radiolysis of cyclohexane containing 0.05 mol.l^{-1} of nitrous oxide. Hydrogen and nitrogen increase linearly with the dose up to 3×10^{20} eV.ml^{-1}, while cyclohexene shows a non-linear dependence on the dose. The initial G-value of

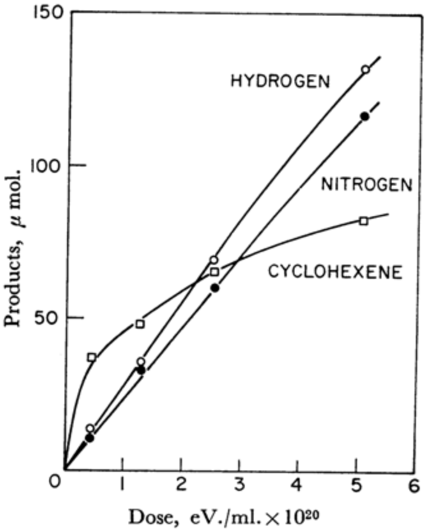

Fig. 1. Dose dependence of the products of the radiolysis of cyclohexane containing 0.05 mol.l^{-1} N_2O.

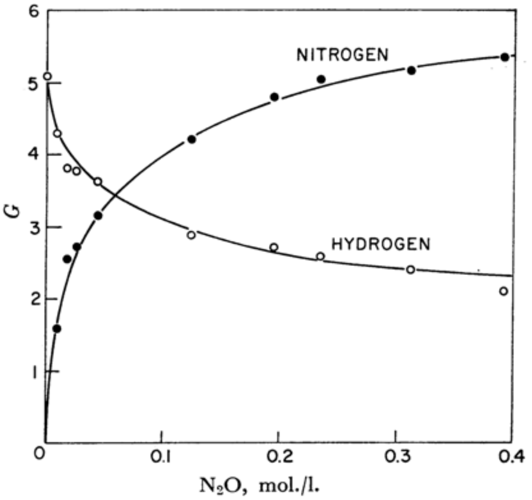

Fig. 2. G-Values of hydrogen and nitrogen from N_2O cyclohexane solution.

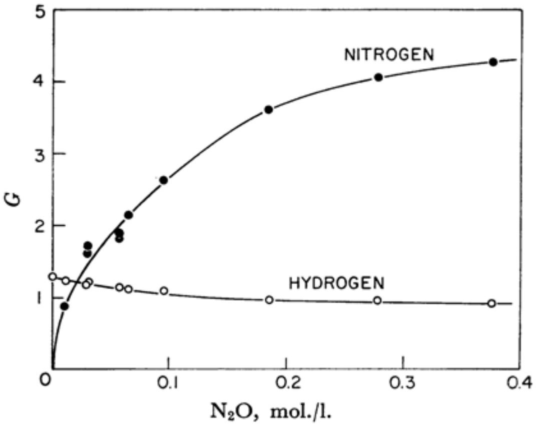

Fig. 3. G-Values of hydrogen and nitrogen from N_2O cyclohexene solution.

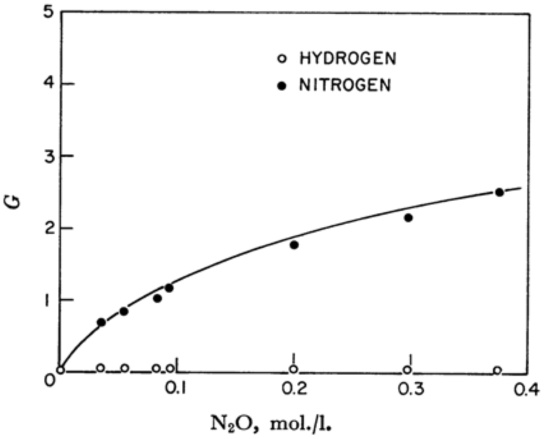

Fig. 4. G-Values of hydrogen and nitrogen from N_2O benzene solution.

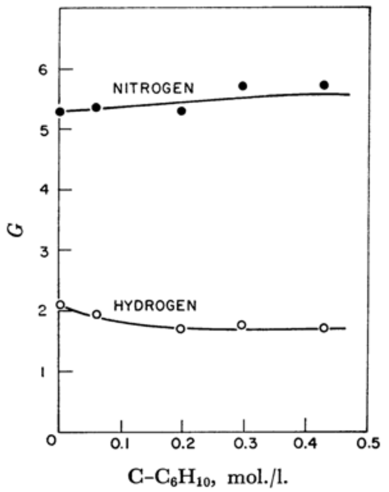

Fig. 5. The effect of cyclohexene on the radiolysis of cyclohexane containing 0.39 mol. l^{-1} N_2O.

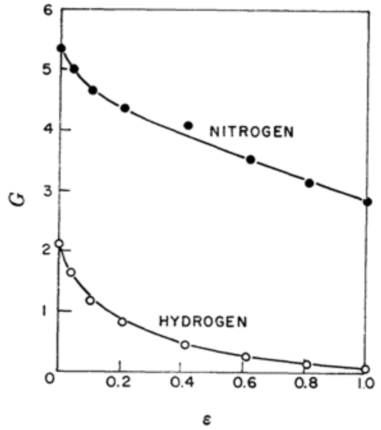

Fig. 6. The effect of N_2O on the radiolysis of mixtures of cyclohexane and benzene. ε is the electron fraction of benzene.

cyclohexene is about twice as large as that in pure cyclohexane.

When the concentration of nitrous oxide is increased, the nitrogen yield increases and the hydrogen yield decreases, though both tend to level-off at high N_2O concentrations, as is shown in Fig. 2. At any N_2O concentration in Fig. 2, the following relationship is found to hold exactly:

$$G(N_2) = 2\Delta G(H_2)$$

where $\Delta G(H_2)$ is the decrease in the G-value of hydrogen. Although quantitative measurements could not be made, the yields of water and cyclohexene were observed to increase with an increase in the concentration of nitrous oxide.

Similar experiments were carried out using cyclohexene and benzene as solvents; the results are shown in Figs. 3 and 4. In these cases water was not detected in the products.

Since olefins are known to act as radical scavengers in the radiolysis of cyclohexane, the effect of the presence of cyclohexene has also been investigated. The results are shown in Fig. 5, where the nitrous oxide concentration is 0.39 mol.l^{-1}. As can be seen from Fig. 2, this concentration is not high enough for $G(N_2)$ and $G(H_2)$ to reach their limiting values. However, in order to obtain a concentration higher than 0.39 mol.l^{-1}, the pressure of N_2O gas inside the cell would have to be in excess of 3 atm., which was the limiting value in the apparatus used.

Figure 6 shows the effect of nitrous oxide on the radiolysis of mixtures of cyclohexane and benzene. The dependence of the nitrogen and hydrogen yields on the electron fraction of benzene evidently indicates an interaction between the two solvents.

Discussion

Nitrous Oxide as an Electron Scavenger.— The initial processes in the radiolysis of cyclohexane may be represented as follows:

$$C_6H_{12}-\begin{cases} \rightsquigarrow C_6H_{12}^+ + e & (1) \\ \rightsquigarrow C_6H_{12}^* & (2) \end{cases}$$

Reaction 1 corresponds to the ionization, and reaction 2 to the excitation, while $C_6H_{12}^*$ does not necessarily mean an excited state of cyclohexane but a precursor of the decomposition into neutral fragments. The nitrous oxide is known to react with electrons as follows:[9]

$$N_2O + e \rightarrow N_2 + O^- \qquad (3)$$

Therefore, if electrons ejected from irradiated cyclohexane are captured by nitrous oxide according to this reaction, the succeeding reactions may be represented as follows:

$$O^- + C_6H_{12}^+ \rightarrow C_6H_{11} + OH \qquad (4)$$

$$OH + C_6H_{12} \rightarrow H_2O + C_6H_{11} \qquad (5)$$

These reactions explain the formation of water and the increase in the G-value of cyclohexene in the radiolysis of a cyclohexane solution.

If reaction 3 is the only source of nitrogen, $G(N_2)$ should be equal to the G-value of the electrons captured by nitrous oxide. At the highest concentration of nitrous oxide used, $G(N_2)$ reaches 5.3, which means that the energy for the formation of an ion pair should be lower than 20 eV. in this system, while the value observed in the gas phase of many hydrocarbons ranges from 20 to 30 eV.,[10] although the value for cyclohexane has not been reported. Another possible source of nitrogen is the reaction of O^- with nitrous oxide; this has been suggested by Johnson and Warman[11] in the gas phase radiolysis of propane:

$$O^- + N_2O \rightarrow N_2 + O_2^- \qquad (6)$$

According to Adams et al.,[12] the rate of the reaction of O^- with the oxygen molecule in an alkaline solution is 2.6×10^9 l. mol^{-1} sec^{-1}. If we take this value for the rate of reaction 6 and assume the rate of reaction of O^- with cyclohexane to be equal to that of a hydrogen atom with cyclohexane, which is lower than 10^7 l.mol^{-1} sec^{-1}, a concentration of 0.1 mol. l^{-1} of nitrous oxide is large enough for the reaction between O^- and cyclohexane to become negligible. However, it is not certain that even a concentration of 0.5 mol.l^{-1} of nitrous oxide is high enough to capture all the electrons ejected from the irradiated cyclohexane.

The highest value of $G(N_2)$ obtained in the radiolysis of cyclohexene solution is 4.3, which is

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[9] G. J. Schulz, *J. Chem. Phys.*, **34**, 1778 (1961).

[10] S. C. Lind, "Radiation Chemistry of Gases," Reinhold Pub. Corp., New York (1961).

[11] G. R. A. Johnson and J. M. Warman, *Nature*, **203**, 73 (1964).

[12] G. E. Adams, J. W. Boag and B. D. Michael, ibid., **205**, 898 (1965).

lower than that for cyclohexane by 1.0. The difference may be explained by the higher reactivity of cyclohexene with O^- than that of cyclohexane.

As is shown in Fig. 5, $G(N_2)$ from a 0.39 mol. l^{-1} N_2O cyclohexane solution slightly increases upon the addition of cyclohexene. The addition of cyclohexene may be considered to assist nitrous oxide in scavenging electrons as follows:

$$e + C_6H_{10} \rightarrow C_6H_{10}^- \qquad (7)$$

$$C_6H_{10}^- + N_2O \rightarrow C_6H_{10} + N_2 + O^- \qquad (8)$$

where $C_6H_{10}^-$ does not necessarily represent a real ion. In other words, cyclohexene provides a shallow trap for electrons. However, this suggestion seems to contradict the observation that $G(N_2)$ from cyclohexene is lower than that from cyclohexane. Evidently, this matter requires further investigation.

Benzene as an Electron Scavenger.—It has recently been established, from studies of the absorption spectra, that aromatic compounds capture electrons to form negative ions; for example, negative naphthalene ions have been observed in the radiolysis at the temperature of liquid nitrogen[13] and diphenyl ions, in the pulsed radiolysis at room temperature.[14] Similarly, benzene may be expected to capture electrons in the radiolysis, although its ability to do so may be weaker. As is shown in Fig. 4, the $G(N_2)$ from a benzene solution of nitrous oxide is about a half of that from a cyclohexane solution at the same concentration of nitrous oxide. This difference may be explained in terms of the competition between nitrous oxide and benzene for electrons. The reactions of benzene may be represented as follows:

$$C_6H_6 + e \rightarrow C_6H_6^- \qquad (9)$$

$$C_6H_6^- + C_6H_6^+ \rightarrow 2C_6H_6 \qquad (10)$$

i. e., some of the electrons ejected from the molecules are captured by benzene to form negative ions, and these ions are then neutralized by their parent ions without decomposing. The ratio of the rates of the competitive reactions, 3 and 9, is estimated to be 20 to 1 from the plots of $G(N_2)$'s in Figs. 4 and 6. The reported value for this ratio is about 100 to 1.[6]

The dependence of $G(H_2)$ on the electron fraction of benzene in Fig. 6 may be tentatively explained by the following charge transfer reaction:

$$C_6H_{12}^+ + C_6H_6 \rightarrow C_6H_{12} + C_6H_6^+ \qquad (11)$$

The possibility of this reaction has already been suggested.[7]

Initial Processes in the Radiolysis of Cyclohexane.—All the important initial steps which can be envisaged in the radiolysis of cyclohexane may be written as follows:

Initial ionization and excitation:

$$C_6H_{12} - \begin{cases} \rightsquigarrow C_6H_{12}^+ + e \\ \rightsquigarrow C_6H_{12}^* \\ \rightsquigarrow C_6H_{12}^{*+} + e \end{cases}$$

Neutralization:

$$C_6H_{12}^+ + e - \begin{cases} \rightarrow C_6H_{12} & (a) \\ \rightarrow H + C_6H_{11} & (b) \\ \rightarrow H_2 + C_6H_{10} & (c) \end{cases}$$

Neutral decomposition:

$$C_6H_{12}^* - \begin{cases} \rightarrow C_6H_{12} & (d) \\ \rightarrow H + C_6H_{11} & (e) \\ \rightarrow H_2 + C_6H_{10} & (f) \end{cases}$$

The decomposition of the excited ion:

$$C_6H_{12}^{*+} - \begin{cases} \rightarrow H + C_6H_{11}^+ & (g) \\ \rightarrow H_2 + C_6H_{10}^+ & (h) \end{cases}$$

where $C_6H_{12}^{*+}$ stands for a precursor ion decomposing before neutralization, if this ever occurs. Reaction h does not necessarily mean a unimolecular decomposition; it can stand for an ion-molecule reaction, such as:

$$C_6H_{12}^+ + C_6H_{12} \rightarrow H_2 + \text{residue} \qquad (12)$$

If we now take the letters $a, b, \ldots$, etc. to represent the G-values for the respective reactions, we can obtain the following simultaneous equations (I to V):

For the case of the radiolysis of pure cyclohexane:

$$G(H_2) = b+c+e+f+g+h = 5.6 \qquad (I)$$

because hydrogen atoms from reactions b, e and g react as follows:

$$H + C_6H_{12} \rightarrow H_2 + C_6H_{11} \qquad (13)$$

and because the observed initial G-value of hydrogen is 5.6.[7]

In the gas phase, the energy needed for the formation of an ion pair of many hydrocarbons is observed to be around 25 eV.; i. e., the G-value of the electron may be assumed to be 4, even in the liquid phase. Therefore:

$$a+b+c+g+h = 4 \qquad (II)$$

The relation observed above, $G(N_2) = 2\Delta G(H_2)$, gives:

$$e+f+g+h = 5.6 - G_e = 1.6 \qquad (III)$$

When cyclohexene is present in sufficient amounts, the reactions involving hydrogen atoms may be omitted; i. e.,

$$G(H_2) = c+f+h = 2.8 \qquad (IV)$$

This value has been estimated to be 2.8 in a previous paper.[7]

When both nitrous oxide and cyclohexene are

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[13] M. R. Ronayne, J. P. Guarino and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

[14] S. Arai and L. M. Dorfman, *J. Chem. Phys.*, **41**, 2190 (1964).

present in sufficient concentrations, the G-value of hydrogen should be given by:

$$G(H_2)=f+h \tag{V}$$

the observed value of which is 1.7, very close to the 1.6 in III. We will now adopt the latter value.

These simultaneous equations give the following solutions:

$$a=e=g=h=0,\ b=2.8,\ c=1.2 \text{ and } f=1.6$$

If this reasoning is correct, the main primary processes in the radiolysis of cyclohexane can be simply expressed as follows, with their approximate G-values as indicated:

$$C_6H_{12} - \begin{cases} \rightsquigarrow C_6H_{12}^+ + e \\ \rightsquigarrow C_6H_{12}^* \end{cases}$$

$$C_6H_{12}^+ + e - \begin{cases} \rightarrow H + C_6H_{11} & G \sim 2.8 \\ \rightarrow H_2 + C_6H_{10} & G \sim 1.2 \end{cases}$$

$$C_6H_{12}^* \rightarrow H_2 + C_6H_{10} \qquad G \sim 1.6$$

The last reaction does not necessarily represent only a unimolecular reaction; it may also include a bimolecular reaction. Deuterium labeling can discriminate between these two possibilities.

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