The Temperature Dependence of the *G*-Values of Nitrogen from the Gas-phase γ-Radiolysis of C_3-Hydrocarbons in the Presence of Nitrous Oxide

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(Received March 6, 1974)

The *G*-values of nitrogen from the gas-phase γ-radiolysis of the C_3-hydrocarbons (propane, propylene, and cyclopropane) in the presence of nitrous oxide have been measured at the temperatures from −35 to 150 °C. The *G*-values increased with an increase in the pressure of N_2O and were saturated at about 4 mol% of N_2O. The saturated values, $G(N_2)_{max}$'s showed characteristic temperature dependences. In propane, they scarcely changed with the temperature and stayed at around 2 G_e. Here G_e is the *G*-value of electrons estimated from the *W*-value of the hydrocarbon. In propylene, the $G(N_2)_{max}$ changed from G_e at −35 °C to about 2 G_e at 150 °C, while in cyclopropane it changed from G_e at −35 °C to 4.5 G_e at 100 °C. Possible reaction mechanisms to explain these results have been discussed.

Nitrous oxide is a well-known electron scavenger.[1,2] When a hydrocarbon is γ-irradiated in the presence of a small amount of nitrous oxide, nitrogen is one of the main products and its formation can be explained by the mechanism initiated by the electron capture of nitrous oxide. The quantitative measurement, however, shows that the *G*-value of nitrogen is always larger than the *G*-value of scavenged electrons. This fact is now one of the most persistent problems in the study of hydrocarbon-radiolysis.[3–7]

In a previous paper,[7] we showed that the *G*-value of nitrogen from the N_2O-1-butene system is strongly dependent upon the temperature as well as on the total dose and the dose rate, and that these effects make the problem more complex. The present paper will report the results obtained with the C_3-hydrocarbons (propane, propylene, and cyclopropane), with which we can make experiments at lower temperatures at the same pressures.

Experimental

The experimental procedure was the same as that reported previously.[7] The temperature of −35 °C was obtained by mixing ice and $CaCl_2$ in a Dewar flask. The temperature lasted (within ±5 °C) long enough for the γ-irradiation, usually three hours.

Results

Figure 1 shows the temperature dependence of the $G(N_2)$'s from the three C_3-hydrocarbons-N_2O systems. Figure 2 shows the $G(H_2)$'s obtained simultaneously with the $G(N_2)$'s. The pressure of hydrocarbons is always around 600 Torr, and the dose rate is 1.3×10^{13} eV ml^{-1} s^{-1}. In order to elucidate the reaction mechanisms, the effects of several additives were also studied. The results are summarized in Table 1.

TABLE 1. THE EFFECTS OF THE ADDITIVES ON THE $G(N_2)$'S FROM THE 4 mol% N_2O–C_3 HYDROCARBON SYSTEMS AT 0 °C

	$G(N_2)$				
	N_2O only	SF_6 0.03 mol %	CO_2 4 mol %	NH_3 4 mol %	CH_3OH 4 mol %
Propane	8.2	0.2	4.4	4.4	20.6
Propylene	5.0	0.3	3.8	4.4	11.1
Cyclopropane	5.9	0.2	3.8	4.4	27.1

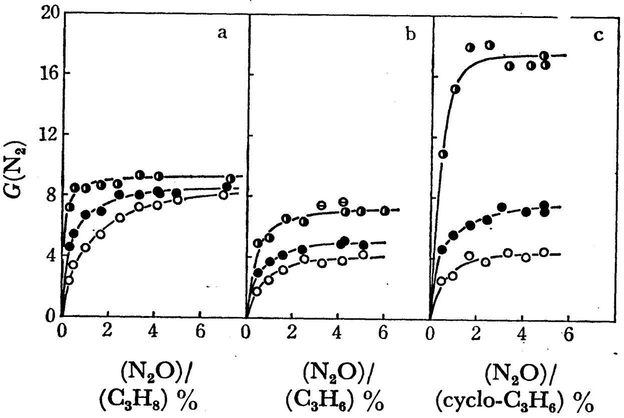

Fig. 1. The temperature dependence of the $G(N_2)$'s from C_3-hydrocarbons in the presence of nitrous oxide. a: propane, b: propylene, c: cyclopropane; ○: −35 °C, ●: 0 °C, ◑: 100 °C, ⊖: 150 °C.

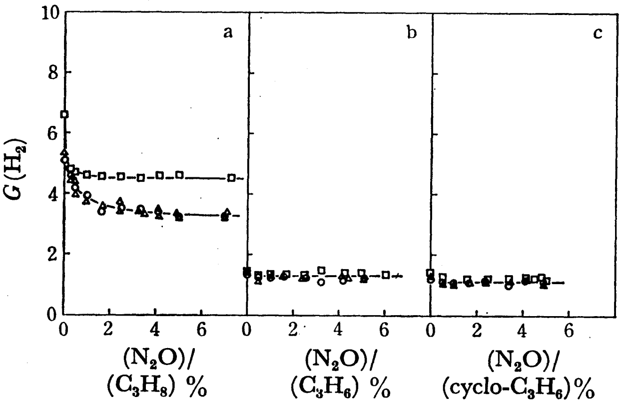

Fig. 2. The temperature dependence of the $G(H_2)$'s from C_3-hydrocarbons in the presence of nitrous oxide. a: propane, b: propylene, c: cyclopropane; ○: −35 °C, △: 0 °C, □: 100 °C.

Discussion

The electrons generated by γ-rays in a high-pressure hydrocarbon will be thermalized very quickly. According to the measurement of Warman and Sauer[8] using a microwave technique, 0.2 Torr of *n*-hexane is high enough to thermalize electrons in a few microseconds. In the present experiment, all the samples contain 600 Torr of C_3-hydrocarbons. The precursor of the nitrogen measured above must be thermalized electrons.[9]

Warman and Fessenden suggested that the electron capture by N_2O occurs through the third-body reaction:[10]

$$e^- + N_2O + M \longrightarrow N_2O^- + M \qquad (1)$$

However, the formation of N_2O^- ions is doubted by many researchers. One of the reasons is that N_2O^- ions have not been observed in the mass-spectrometric study at low pressures of N_2O.[11] The reaction might be:

$$e^- + N_2O \xrightarrow{(+M)} N_2 + O^- \qquad (2)$$

The present experiment cannot specify the reaction.

In a previous paper,[7] we proposed this reaction:

$$N_2O^- + SF_6 \longrightarrow N_2O + SF_6^- \qquad (3)$$

to explain the fact that a very small amount of SF_6 can inhibit the formation of nitrogen from the N_2O-hydrocarbon systems. However, according to the recent paper of Bansal and Fessenden,[12] the electron capture of SF_6 is extremely fast (2×10^{-7} cm^3 mol^{-1} s^{-1}). If this is true, the inhibition effect can be explained simply by the competition of N_2O and SF_6 for thermalized electrons.

In the following discussion, we will assume that N_2O^- ions, even if produced, react much as do O^- ions. When O^- (or N_2O^-) ions are produced in propane, the following reaction will occur very readily:

$$O^- + C_3H_8 \longrightarrow OH^- + C_3H_7 \qquad (4)$$

The rate of Reaction (4) has been reported to be 9.3×10^{-10} cm^3 mol^{-1} s^{-1}.[13] Since the OH^- ions thus formed are stable ions as far as they are not neutralized (the neutralization time at the dose rate used here is estimated to be 10^{-3} s), the following addition reaction may occur:

$$OH^- + N_2O \longrightarrow OHN_2O^- \qquad (5)$$

This reaction has been proposed by Parkes[14] on the basis of the mass-spectrometric observation that the principal product in the N_2O–C_2H_6 system is the mass 61, OHN_2O^-.

In our propane case, therefore, the main neutralization reaction may be:

$$OHN_2O^- + C_3H_8^+ \longrightarrow N_2 + C_3H_7 + 2OH \qquad (6)$$

If this mechanism is correct, we can understand the $G(N_2)\simeq 2G_e$ relation, which should be independent of the temperature examined. If NH_3, the dipole moment of which is larger than that of N_2O, is present, Reaction (5) will be interrupted by the clustering of NH_3 on the OH^- ion. This is in accord with the observation that the addition of NH_3 to the N_2O-hydrocarbon system decreased the $G(N_2)_{max}$'s to G_e, as shown in Table 1.

When propylene is the substrate, there are two possible processes in the reaction of O^- ions, because they are mono-radicals:

$$\begin{aligned} CH_3CH{=}CH_2 + O^- &\longrightarrow \underset{\cdot}{C}H_2CH{=}CH_2 + OH^- &(7)\\ &\searrow CH_3\underset{\cdot}{C}H{-}CH_2{-}O^- &(8)\end{aligned}$$

Process (8) may be a third-body reaction, and the product ions may not contribute to the formation of nitrogen. By analogy to the reactions of monoradicals with olefins, Process (7) will have a certain amount of activation energy, while the activation energy of Process (8) may be nearly zero. Taking these reactions into account, the temperature dependence of the $G(N_2)_{max}$ in propylene may be expressed as follows:

$$\frac{G(N_2)_{max}}{G_e} = 1 + \frac{A\exp(-E_7/RT)}{1+A\exp(-E_7/RT)}$$

Here, E_7 represents the activation energy of Process (7). A is the ratio of the pre-exponential factors of Processes (7) and (8). The curve shown in Fig. 3 is drawn by assuming that $E_7=4.7$ kcal mol^{-1} and $A=2.8\times10^2$. These values are not unreasonable for a radical reaction.[15]

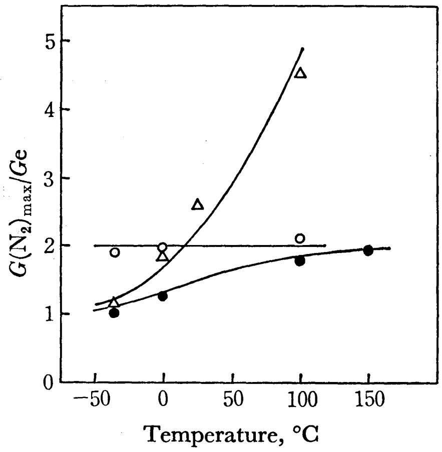

Fig. 3. The temperature dependence of the $G(N_2)_{max}$'s
○: propane, ●: propylene, △: cyclopropane.

In the case of cyclopropane, much more speculation has to be undertaken, because very few reports have been published on the reactions of cyclopropane. The results described above obviously show the chain decomposition of N_2O. One possible chain reaction is as follows:

$$O^- + \text{cyclo-}C_3H_6 \longrightarrow CH_2O^- + C_2H_4 \qquad (9)$$

$$CH_2O^- + N_2O \longrightarrow CH_2O + N_2 + O^- \qquad (10)$$

The apparent activation energy for the formation of nitrogen was calculated to be 3.6 kcal mol^{-1} by using this equation:

$$G(N_2)_{max}/G_e = 1 + A_9\exp(-E_9/RT)$$

Here, A_9 and E_9 are the pre-exponential factor and the activation energy of Process (9) respectively.

The addition of CO_2 to the 4 mol% N_2O–C_3-hydrocarbon systems reduced the $G(N_2)$'s to around G_e, irrespective of the C_3-hydrocarbons. Such an effect has already been reported by Warman;5) it may be interpreted in terms of this reaction:

$$O^- \text{ (or } N_2O^-) + CO_2 \longrightarrow CO_3^- \ (+N_2) \qquad (11)$$

The effect of CH_3OH on the $G(N_2)$'s is obviously different from those of other additives. In the radiolysis of pure methanol, it has already been recognized that, when N_2O is added to the system, nitrogen is produced in a chain reaction.16) Although CH_3OH has been used as a positive ion-interceptor in the liquid-phase radiolysis, its effect is obviously not so simple in the gas-phase.

References

1) G. Scholes and M. Simic, *Nature*, **202**, 895 (1964).

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

3) W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1661 (1967); *J. Phys. Chem.*, **71**, 2562 (1967).

4) S. J. Rzad and J. M. Warman, *ibid.*, **72**, 3013 (1968).

5) J. M. Warman, *ibid.*, **71**, 4066 (1967).

6) G. R. A. Johnson and J. L. Redpath, *Trans. Faraday Soc.*, **66**, 861 (1970).

7) K. Okazaki, R. Yugeta, and S. Sato, This Bulletin, **46**, 2066 (1973).

8) J. M. Warman and M. C. Sauer, Jr., *J. Chem. Phys.*, **52**, 6428 (1970).

9) By using the equation proposed for the thermalization of electrons in *n*-hexane, the thermalization time at 600 Torr is estimated to be 10^{-10} s, while the lifetime in the presence of N_2O, which captures electrons, can be calculated to be longer than 10^{-4} s.10)

10) J. M. Warman and R. W. Fessenden, *J. Chem. Phys.*, **49**, 4718 (1968).

11) J. L. Moruzzi and J. T. Dakin, *ibid.*, **49**, 5000 (1968).

12) K. M. Bansal and R. W. Fessenden, *ibid.*, **59**, 1760 (1973).

13) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, **47**, 2715 (1969).

14) D. A. Parkes, *J. Chem. Soc. Faraday I*, **68**, 2103 (1972).

15) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," Vol. 1, ed. by G. Porter, Pergamon Press, Oxford (1961), p. 105.

16) M. Meaburn and F. W. Mellows, *Trans. Faraday Soc.*, **61**, 1701 (1965).