The *G*-values of Nitrogen Obtained from the Gas-phase γ-Radiolysis of Nitrous Oxide–Hydrocarbon Systems

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The gas-phase γ-radiolysis of a N_2O–1-butene system has been reinvestigated. The other hydrocarbons used for the substrate are ethylene, propylene, 1,3-butadiene, cyclopropane, propane, and *n*-butane. The *G*-value of nitrogen from any system increased with an increase in the pressure of N_2O and was saturated at about 4 mol% of N_2O. The saturated value, $G(N_2)_{max}$, was much larger than the *G*-value of electrons estimated from the *W*-value of the hydrocarbon used and was rather strongly dependent upon the irradiation temperature, the dose rate, and the total dose. Some of the results were not consistent with those reported by the previous investigators. The reason for this discrepancy, and also the possible reaction mechanism to explain the large $G(N_2)_{max}$, have been discussed.

Nitrous oxide has been used as an electron scavenger in the gas- and liquid-phase radiolyses of hydrocarbons.[1-3] If the yield of nitrogen is consistent with the amount of scavenged electrons, we can study many features of the radiolysis. Generally, however, the *G*-value of nitrogen from the gas-phase radiolysis of a hydrocarbon in the presence of nitrous oxide is higher than that to be expected from the *W*-value of the hydrocarbon. This excess nitrogen yield has usually been explained in terms of the reactions between nitrous oxide and negative species produced in the electron-scavenging reaction of nitrous oxide.

According to the paper of Warman,[4] there are two groups of alkenes. One consists of isobutene and propylene, which give $G(N_2)_{max}=G_e$. Here, $G(N_2)_{max}$ is the maximum *G*-value of nitrogen which results from the electron scavenging of nitrous oxide and G_e is the *G*-value of electrons, as estimated from the *W*-value of the hydrocarbon. The other group consists of 1-butene and *cis*- and *trans*-2-butene, which give $G(N_2)_{max}=2\,G_e$. On the other hand, in the gas-phase radiolysis of alkanes (C_2, C_3, and C_4), $G(N_2)_{max}=1.55\,G_e$ has been reported. The data so far introduced were obtained at room temperature.

Holtslander and Freeman[5] reported that, in the γ-radiolysis of methylcyclohexane at 110 °C, the *G*-value of nitrogen attains as high as $5\,G_e$; they attributed this high yield to the ionic chain reaction between the oxygen atom ion and the hydrocarbon. In the case of the benzene-nitrous oxide system at room temperature, the $G(N_2)_{max}$ is reported to be 8.2 G_e, and the $G(C_6H_5OH)$, to be 6.4 G_e.[6] The authors explained this result in terms of the chain reaction including $C_6H_6O^-$ as the chain carrier.

The present authors hoped to find a more systematic explanation of these rather conflicting data, and so reinvestigated the gas-phase γ-radiolysis of 1-butene in the presence of nitrous oxide. For comparison, several experiments were performed with ethylene, propylene, 1,3-butadiene, cyclopropane, propane, and *n*-butane.

Experimental

The nitrous oxide (Showa Denko Co.), ethylene, propylene 1-butene, propane, *n*-butane, cyclopropane, 1,3-butadiene (Takachiho Chemical Co.), and sulfur hexafluoride (Matheson Co.) were used after several bulb-to-bulb distillations. The volume of the irradiation cell was 50 ml. Before preparing the irradiation sample, the cell was heated with a torch under a vacuum. The pressure of the hydrocarbon was around 600 Torr in all the experiments. The irradiation temperatures were 0 °C, room temperature, and 100±1 °C.

For the measurement of the dose rate, use was made of the Fricke dosimeter. In order to check the difference between the gas-phase radiolysis and the liquid one, the radiolysis of ethylene was carried out. The obtained *G*-value of hydrogen from ethylene was 1.30±0.02, which is in agreement with the literature value, 1.31.[7]

The amount of the non-condensable products at 77 K (N_2, H_2, and CH_4) was measured with a Toepler pump equipped with a gas buret. This non-condensable gas was passed through a furnace of cuprous oxide at 300 °C in order to combust the hydrogen into water, which was then trapped at 77 K. After the measurement of the amount, the remaining gas was analyzed by mass spectrometry.

Results

Figure 1 shows the *G*-values of nitrogen as a function of the mol% of nitrous oxide. The hydrocarbons used are propylene, ethylene, 1,3-butadiene, and cyclopropane. The pressure is 600 Torr, and the irradiation temperature is room temperature. The dose rate used here is 2×10^{-13} eV ml^{-1} sec^{-1}. As may be seen in Fig. 1, the $G(N_2)_{max}$'s are 6.5 for propylene, 9.2 for ethylene and 1,3-butadiene, and 10.3 for cyclopropane. The data obtained with 1-butene is not shown because of considerable scattering, although the $G(N_2)_{max}$ was found in the range from 12 to 13. It may be worthwhile to mention here that the $G(N_2)_{max}$ values for propylene and for 1-butene are 1.5 times larger than those reported by Warman.[4]

Since we found considerable scattering data in the

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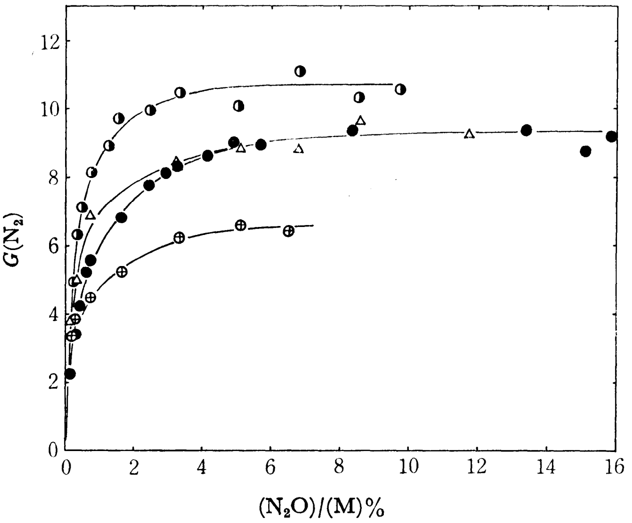

Fig. 1. G-values of nitrogen from N_2O–hydrocarbon systems as a function of the $[N_2O]/[M]$ ratio. △: ethylene, ⊕: propylene, ●: 1,3-butadiene, ◑: cyclopropane.

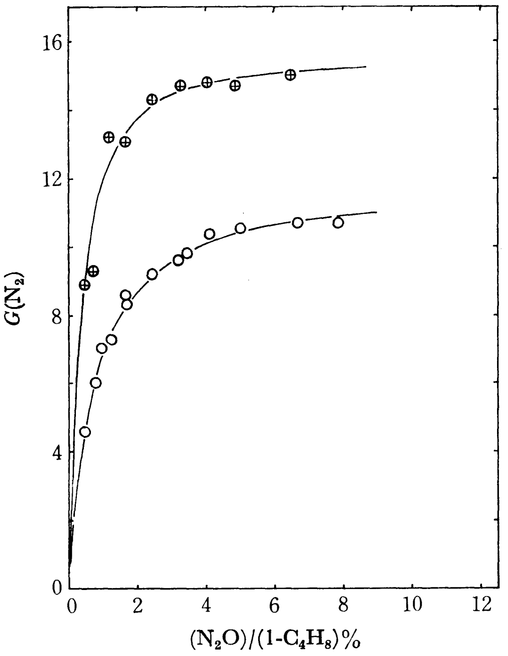

Fig. 2. G-values of nitrogen from a N_2O–1-butene system as a function of the $[N_2O]/[1\text{-butene}]$ ratio.
○: 0 °C, ⊕: 100 °C.

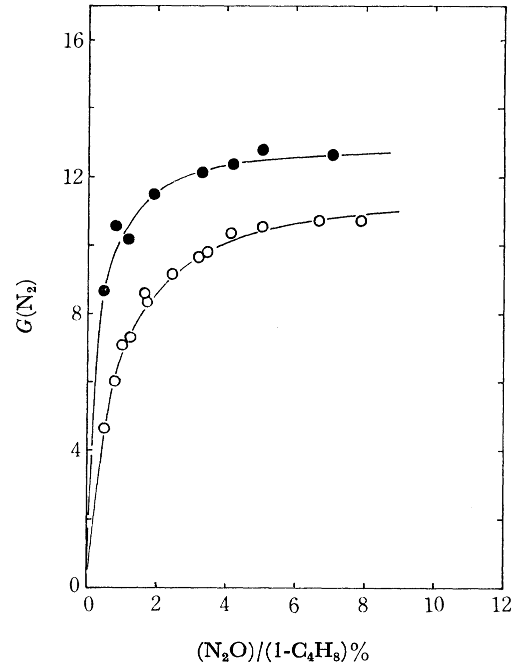

Fig. 3. The effect of dose rate on the G-value of nitrogen from a N_2O–1-butene system. ○: 1.9×10^{13} eV ml^{-1}s ec^{-1}, ●: 3.6×10^{12} eV ml^{-1} sec^{-1}.

TABLE 1. $G(N_2)_{max}$ FROM N_2O–HYDROCARBON SYSTEMS AND THE EFFECT OF THE ADDITION OF SF_6

Substrate (600 Torr)	$G(N_2)_{max}$ Room temperature This work	$G(N_2)_{max}$ Room temperature Literature values	$G(N_2)_{max}$ 0 °C This work	$G(N_2)$ in the presence of 0.03 mol % SF_6 at 0 °C
Propane	—	7.5,[3] 6.5,[4] 8.7[20]	8.2	0.2
n-Butane	—	6.5[4]	8.8	0.3
Ethylene	8.7	—	8.0	0.2
Propylene	6.3	4.2[4]	5.0	0.3
1-Butene	14.8[a]	8.4[4]	10.4	0.3
Cyclopropane	10.4	—	7.3	0.2
1,3-Buradiene	8.6	—	6.2	0.1

a) Obtained at 100 °C.
b) $G(N_2)$ from a 4.1 mol% N_2O–hydrocarbon system.

case of 1-butene, we controlled the irradiation temperatures at 0 and 100 °C. Figure 2 shows the results. From this figure, we can understand that the G-value of nitrogen is rather strongly temperature-dependent.

The dose rate-dependence of $G(N_2)$ from the N_2O–1-butene system has also been investigated. The results are shown in Fig. 3. The dose rates are 1.9×10^{13} and 3.6×10^{12} eV ml^{-1} sec^{-1}. The irradiation temperature is 0 °C, and the total dose is 1.9×10^{17} eV ml^{-1}. The $G(N_2)_{max}$ values are 10.7 for the higher dose rate and 12.7 for the lower. When the total dose was changed from 1.9×10^{17} to 9.6×10^{17} eV ml^{-1}, the $G(N_2)_{max}$ decreased from 10.3 to 8.4. With doses lower than 1.9×10^{17} eV ml^{-1}, the $G(N_2)_{max}$ did not change from 10.3.

Table 1 summarizes the $G(N_2)$'s from seven hydrocarbons containing 4.1 mol% nitrous oxide at 0 °C, along with the values at room temperature and the $G(N_2)$'s in the presence of 0.03 mol% SF_6. The dose rate and the total dose used here are 1.9×10^{13} eV ml^{-1} sec^{-1} and 1.9×10^{17} eV ml^{-1}.

Since the dosimetry by the decomposition of nitrous oxide plays an important role in the explanation of the present results, we measured the $G(N_2)$ from pure nitrous oxide at three different temperatures. The results are summarized in Table 2, together with the

Table 2. $G(N_2)$ from pure N_2O

$G(N_2)$	Source	Temperature	Reference
12.0	^{60}Co γ	room	Johnson
10.9	4 MeV X	room	Hearne
11.25	T β	room	
10.0	^{210}Po α	25 °C	Sears
7.6	^{222}Rn α	25 °C	
9.9	^{60}Co γ	10 °C	
10.0	1 MeV e$^-$	24 °C	Jones
12.4		70 °C	
14.1		100 °C	
17.9		150 °C	
21.1		200 °C	
10.1	^{60}Co γ	room	Takao
10.9	^{60}Co γ	room	This work
9.3		0 °C	
12.5		100 °C	

data of previous workers.[8–12] The obtained temperature dependence was very similar to that reported by Jones and Sworski,[11] who used 1 MeV electrons from a Van de Graaff apparatus as the irradiation source. Our data were independent of the dose rate used in the range from 2.8×10^{12} to 1.5×10^{13} eV ml^{-1} sec^{-1}.

Discussion

Accumulating evidence[13–19] seems to establish that a third-body reaction is necessary for thermalized electrons to attach to nitrous oxide. According to Warman and Fessenden,[18] the rate constant of this third-body reaction at 300 K is $5.6\pm0.2\times10^{-33}$ ml^2 molecules^{-2} sec^{-1}, while Johnson and Redpath[13] estimated it to be 2×10^{-31} ml^2 molecules^{-2} sec^{-1}. On the other hand, Holtslander and Freeman[5] estimated the lifetime of the decomposition of N_2O^- into N_2 and O^- in the atmosphere of methylcyclohexane at 110 °C to be in the range from 10^{-4} to 10^{-3} sec.

As is shown in Table 1, the presence of a very small amount of SF_6, a well-known electron scavenger, suppressed the formation of nitrogen from the γ-radiolyses of seven hydrocarbons containing 4.1 mol% N_2O. The precursor of nitrogen, therefore, must be thermalized electrons. A pressure of 600 Torr of hydrocarbons is probably high enough to thermalize electrons before the occurrence of the dissociative electron-capture process of N_2O.

The reactions of electrons in the present system, therefore, may be expressed as follows:

$$e^- + N_2O \xrightarrow{+M} N_2O^- \tag{1}$$

$$e^- + M^+ \longrightarrow \text{products} \tag{2}$$

Here, M and M$^+$ stand for a hydrocarbon molecule and its positive ion. The G-values of electrons estimated from the W-values of hydrocarbons are to be around 4; accurate values are known for propane (4.27), n-butane (4.37), ethylene (3.86), propylene (4.03), and 1-butene (4.10).[7] Therefore, all of the $G(N_2)_{\max}$ values obtained in the present experiment are larger than the G_e's. The excess nitrogen yield ranges from 0.25 G_e for propylene at 0 °C to 2.5 G_e for 1-butene at 100 °C.

As Table 1 shows, there are rather serious discrepancies between the $G(N_2)_{\max}$ reported by Warman and his co-workers[3,4,20] and ours. Therefore, we carefully compared their experimental conditions with ours—the dose rate, the total dose, the pressure of the sample, the irradiation temperature, and so on, but we could not find the reason for this discrepancy. The ethylene dosimetry has also been checked; they used $G(H_2)=1.31$, which is in good agreement with our result, $G(H_2)=1.30\pm0.02$. Since most of their experiments were carried out with a cell of about 150 ml, while ours was 50 ml, we also used the same-size cell as theirs; however, the data we thus obtained were the same as those observed with the 50 ml cell. The question of the discrepancy in the $G(N_2)_{\max}$ value, therefore, is still open.

In the studies of the γ-radiolysis of propane containing N_2O, Warman reported $G(N_2)_{\max}=7.5$,[3] 6.5,[4] and 8.7.[20] The difference between 6.5 and 7.5 is probably due to the dose-rate dependence, although they did not mention it. The large value of 8.7 probably resulted from the nitrous oxide dosimetry; Warman used $G(N_2)=12.0$, but the most reliable G-value at present is 10.0 at room temperature.[11] According to the present measurements, the $G(N_2)$ from the 4.1 mol% N_2O–propane system at 0 °C is 8.2, larger than that reported by Warman. Recently, Johnson and Redpath.[13] reported $G(N_2)=7.5$ from the 2 mol% N_2O–propane system. This result is in accord with ours.

In order to explain the excess nitrogen yield observed in the present experiment, we propose the following reaction scheme:

$$\begin{array}{lll} N_2O^- + M & \longrightarrow N_2 + X^- & a \\ & \searrow N_2 + P^- & 1-a \end{array} \tag{3}$$

$$X^- + N_2O \longrightarrow N_2O^- + \text{residue} \tag{4}$$

$$N_2O^- + M^+ \longrightarrow N_2 + \text{residue} \tag{5}$$

$$P^- + M^+ \longrightarrow \text{products} \tag{6}$$

Here, a is the branching ratio of the reactions of N_2O^- with a hydrocarbon. X^- and P^- are unspecified ions, which we will discuss below. The essential difference between the X^- and P^- ions in the above scheme is that X^- can react readily with N_2O to produce its ion, while P^- cannot. In this scheme, we have excluded

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the neutralization reaction between X^- and M^+ ions. As is shown in Table 1, 0.03 mol% SF_6 was effective enough to suppress the formation of nitrogen. This suggests that the following charge-transfer reaction:

$$N_2O^- + SF_6 \longrightarrow N_2O + SF_6^-$$

takes place very readily and that, in the presence of 0.03 mol% SF_6, this reaction occurs much faster than the neutralization reaction, Reaction (5). If X^- ions are very reactive to N_2O, the neutralization reaction between X^- and M^+ ions may be ignored in the presence of a certain amount of N_2O.

Recently, Bohme and his co-workers[21,22] observed the reactions between O^- ions and several hydrocarbons by using the afterglow method and reported that their specific rates are of the order of 10^{-9} ml molecules^{-1} sec^{-1}:

$$\begin{array}{lll} O^- + RH \longrightarrow & R^- + OH & a' \\ \qquad\qquad\searrow & OH^- + R & 1-a' \end{array}$$

They also showed that the branching ratio of these two reactions is strongly dependent on the kind of hydrocarbon. Reaction (3) in the above reaction scheme is analogous with this reaction.

The steady-state treatment based on Reactions (1)~(6) gives the following relationship:

$$\frac{1}{G(N_2)} = \frac{1}{G(N_2)_\infty}\left(1 + \frac{k_2}{\sqrt{k_a k_1}}\sqrt{\frac{D}{W}}\frac{1}{[N_2O]}\right) \qquad (I)$$

Here,

$$k_a = \frac{k_2[e^-] + k_6[P^-]}{[e^-] + [P^-]}$$

and D stands for the dose rate, and *W*, for the *W*-value of the hydrocarbon used. $G(N_2)_\infty$ is the *G*-value of nitrogen when all of the ejected electrons are scavenged by N_2O. By using the pulse radiolysis technique, Lias *et al.*[23] measured the rates of the neutralization of the *t*-butyl ion by an electron and by the SF_6^- ion, and reported $k(t\text{-}C_4D_9^+ + e^-) = 1.92 \times 10^{-6}$ ml molecules^{-1} sec^{-1} and $k(t\text{-}C_4D_9^+ + SF_6^-) = 4.0 \times 10^{-7}$ ml molecules^{-1} sec^{-1}. If we take these values for our k_2 and k_6 respectively, the k_a value may be said to be in between those two values.

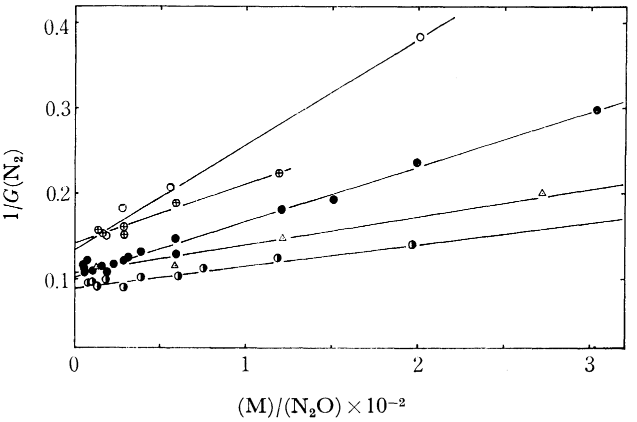

Fig. 4. Plots for Eq. (I). ○: 1,3-butadiene at 0 °C, ●: 1,3-butadiene at r. t., △: ethylene, ⊕: propylene, ◑: cyclopropane.

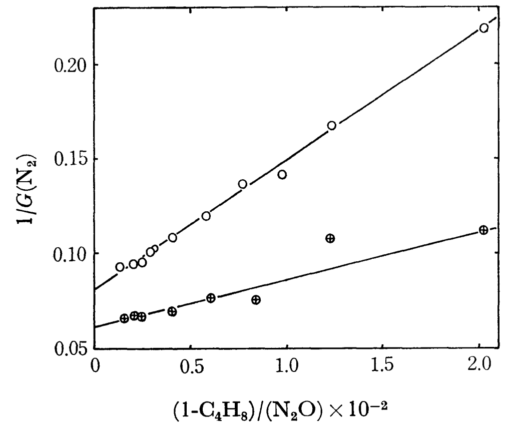

Fig. 5. Plots for Eq. (I) on 1-butene. ○: 0 °C, ⊕: 100 °C.

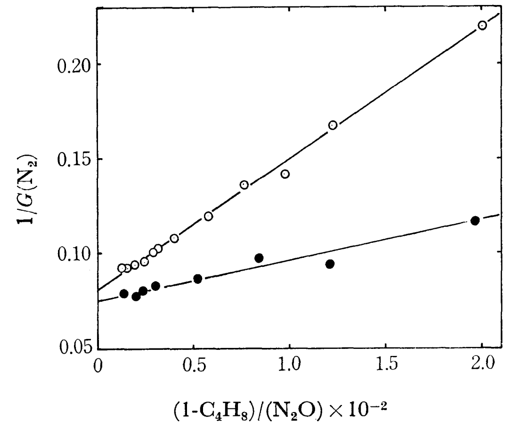

Fig. 6. Plots for Eq. (I), on 1-butene.
○: 1.9×10^{13} eV ml^{-1} sec^{-1}, ●: 3.6×10^{-12} eV ml^{-1} sec^{-1}.

Table 3. Calculated values of $G(N_2)_\infty$ and *a*

Substrate	Dose rate eV ml^{-1} sec^{-1}	$G(N_2)_\infty$	$k/(\sqrt{k_a k_1})$ (molec· ml^{-1} sec)$^{1/2}$	*a*	
1-Butene	1.9×10^{13}	12.1	1.7×10^{11}	0.71	0 °C
	3.6×10^{12}	13.2	1.4×10^{11}		
	1.8×10^{13}	16.0	8.3×10^{10}	0.78	100 °C
1,3-Butadiene	1.8×10^{13}	7.9	2.2×10^{11}	0.51	0 °C
	2.1×10^{13}	9.9	1.3×10^{11}	0.62	room temp.
Ethylene	1.1×10^{13}	9.2	1.1×10^{11}	0.60	
Propylene	1.6×10^{13}	7.2	1.3×10^{11}	0.46	
Cyclopropane	2.0×10^{13}	11.1	7.2×10^{10}	0.67	

Figure 4 shows the plots of $1/G(N_2)$ against the $[M]/[N_2O]$ ratio, where M's are ethylene, propylene, 1,3-butadiene, and cyclopropane. Figures 5 and 6 show the results obtained with 1-butene. From these linear relationships, we can calculate $G(N_2)_\infty$ and $k_2/(\sqrt{k_a k_1})$, which are summarized in Table 3. All of the $k_2/(\sqrt{k_a k_1})$ values are of the order of 10^{11} (molecules ml^{-1} sec)$^{1/2}$. From this value, the third-body reaction rate of Reaction (1) can be estimated to be 10^{-33} ml^2 molecules^{-2} sec^{-1} by assuming $k_a = 10^{-6}$ ml mole-

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cules^{-1} sec^{-1} and by taking into account the fact that the pressure of hydrocarbons used in the present experiment is 600 Torr. The estimated value, 10^{-33}, may be compared with that of 5.6×10^{-33} reported by Warman and Fessenden.[18]

From the reaction scheme proposed above, this relationship:

$$\frac{G_e}{G(N_2)_\infty} = 1 - a\left(1+\frac{k_5}{\sqrt{k_a k_3}}\sqrt{\frac{D}{W}}\frac{1}{[M]}\right)^{-1} \tag{II}$$

can also be derived. In the case of 1-butene at 0 °C, we have a pair of data on the $G(N_2)_\infty$ for two different dose rates. The substitution of these data into Eq. (II) gives:

$$a = 0.71$$

and: $$\frac{k_5}{\sqrt{k_a k_3}} = 1.1\times10^{12}\ (\text{molecules ml}^{-1}\ \text{sec})^{1/2}.$$

If we can assume the value of 1.1×10^{12} even for other hydrocarbons and for different temperatures, we can calculate the a values for other hydrocarbons. These values are also listed in Table 3. The accuracy of these numbers is open to further investigation, but we believe that these values can become an index for estimating the $G(N_2)_\infty$.

Speculations for X^- and P^- Ions. When olefins are used as the substrate, Reactions (3) and (4) may be written as follows, by analogy with the O^- reactions:[21]

$$\begin{array}{llll} N_2O^- + RH & \longrightarrow & N_2 + R^- + OH & a \\ & \searrow & N_2 + R + OH^- & 1-a \end{array} \tag{3'}$$

$$R^- + N_2O \longrightarrow N_2O^- + R \tag{4'}$$

As has been shown above, the branching ratio, a, obtained with 1-butene at 0 °C was 0.71, which is not inconsistent with the a' value, 0.6 ± 0.1, reported by Bohme *et al.* However, in the case of propylene, the a value was 0.46, while the a' value was reported to be 0.05 ± 0.05. A more serious difference was observed in the case of ethylene. According to Bohme *et al.*, the reaction between O^- ions and ethylene gives ethylene oxide and electrons. We checked the presence of ethylene oxide in the products of the γ-radiolysis of C_2H_4 containing N_2O, but we could not observe it by gas chromatography. The only product we could observe, except nitrogen, was water, although we did not measure it quantitatively.

In the case of paraffins, the a' values have been reported to be zero.[22] If the a values are also zero, the $G(N_2)_{max}$ cannot be more than the G_e's. The experimental results obviously contradict this. One possible explanation for this contradiction, and also for the discrepancy between the a and a' values for propylene and ethylene, is that the reaction between N_2O^- ions and RH produces the excited OH^{-*} ions, which can then react with other RH's to produce R^- ions.

In order to establish the reaction mechanism of the formation of nitrogen, it is necessary to continue further investigations, probably using a different approach.