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Effect of Polar Molecules on Reaction of Negative Ions in Radiolysis of Hydrocarbon + Nitrous Oxide Systems in the Gas Phase

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In the radiolysis of gaseous hydrocarbons containing small amounts of N₂O (2 mol %) the radiation-produced electrons react with N₂O leading eventually to $G(N_2) > G_e$. In the presence of polar molecules with low electron affinity (H₂O, NH₃, CH₃Cl) a limiting value of $G(N_2) = G_e$ could be reached depending on the concentration of the polar compound and the temperature of the system. It is suggested that the clustering of O⁻ (or N₂O⁻) in addition to proton transfer inhibits the formation of the excess nitrogen yield ($\Delta G(N_2) = G(N_2) - G_e$). At temperatures above 80° $G(N_2) = 2G_e$.

Introduction

Interaction between ionic species produced in the gas phase and molecules with large dipole moments was recognized not long after the discovery of ionization phenomena. It was successfully applied in Wilson cloud chambers where either alcohol or water molecules formed large visible clusters around the ions produced by the passage of ionizing particles. Ion mobility measurements produced many discordant results due to the presence of small amounts of impurities. The low values of mobility of various positive and negative ions were later attributed to cluster formation.²

The initial step, *i.e.*, the formation of clusters with small numbers of molecules, has been neglected for a long time and only recently, with the development of high-pressure mass spectroscopy, has this process attracted due attention. Quantitative data such as ΔH , ΔG , and ΔS have been obtained for each particular step,³ in several systems for positive ions and only very recently for some negative ones.⁴

The role of clusters in radiation chemistry was discussed by Lind⁵ as early as 1919, but it was not accepted because of the lack of conclusive evidence. It was proposed, more recently, that the decomposition of neutralized H₃O⁺ and NH₄⁺ ions depends on the size of their clusters.⁶ Unfortunately, other complicating factors, mainly chain thermo-radiolytic decomposition of the

organic component, tend to cast some doubt on these conclusions.⁷

In this work we present some results indicating the formation of clustered O⁻ or N₂O⁻ ions and discuss a few specific reactions which discriminate between the clustered and bare negative ions.

Experimental Section

All irradiations were carried out in annular Pyrex vessels (~340 ml) fitted with break-seals. Prior to use vessels were baked in air at ~500° for a day and then pumped at least for 0.5 hr down to <10⁻⁵ Torr. Desired amounts of gases were introduced by condensing from gas sample vessels filled at required PVT. Pure

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(2) L. B. Loeb, "Basic Processes of Gaseous Electronics," University of California Press, Berkeley and Los Angeles, Calif., 1961.

(3) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).

(4) (a) P. Kebarle, M. Arshadi, and J. Scarborough, *J. Chem. Phys.*, **49**, 817 (1968); (b) P. Kebarle, S. R. Searles, A. Zolla, J. Scarborough, and M. Arshadi, 25th International Mass Spectrometry Conference, Berlin, 1967.

(5) S. C. Lind, *J. Amer. Chem. Soc.*, **41**, 531 (1919).

(6) A. R. Anderson, B. Knight, and J. A. Winter, *Nature*, **209**, 199 (1966); A. R. Anderson and J. A. Winter, "The Chemistry of Ionization and Excitation," Taylor and Francis, Ltd., 1967, p 197.

(7) G. R. A. Johnson and M. Simic, *Nature*, **212**, 1570 (1966).

water was weighed and degassed by freezing and pumping. Care was taken not to lose water as an aerosol. It was also introduced into one vessel by distillation at 77°K. The vessels were sealed at 77°K while opened to the vacuum system.

Water was purified by distilling first from alkaline potassium permanganate and then redistilled. Dry ammonia, methyl chloride, dimethyl ether, SF₆ (Matheson Gases), propane (Phillips Research grade), and N₂O (British Oxygen Gases, medical grade) were condensed at 77°K and degassed by several thawing-freezing-pumping cycles. They were also distilled from Dricold traps and only the middle fraction taken to remove the possible traces of water. Cyclohexane (Phillips Research grade) was used without further purification.

The vessels were irradiated by a 1-kCi ⁶⁰Co source. Before irradiating the vessels were thermally equilibrated at the desired temperature, either in an oven or a freezer around the source, which were controlled to ±2°.

The dose rate was measured by N₂O dosimeter taking $G(N_2) = 10.0$.⁸ (The same value was obtained by G. R. A. Johnson and M. Simic, unpublished results.) The energy absorbed in various components of the gas mixture, E_x , was calculated from energy absorbed in N₂O, E_n , using the relation of stopping powers per molecule obtained by Meisels.⁹ For those gases where data were not available, it was assumed that energy absorbed in each gas was proportional to its electron density. The energy in the mixture, E_t , was taken as the sum of the energies absorbed in the components. The average dose rate in this particular type of vessel filled at 1 atm with propane was 1.84×10^{13} eV ml⁻¹ sec⁻¹. All irradiations were carried out at total pressure 1–1.1 atm. The total dose was in the region of 1.8×10^{19} to 5.4×10^{19} eV.

The radiation-produced gases which were not condensable at 77°K were quantitatively pumped into a gas buret and the PVT readings taken. The composition of the gas was determined mass spectrometrically either on AEI MS 3 or on the high-resolution MS 9.

Results

All results are expressed in G values. $G(X)_t$ and $G(X)_i$ are the number of molecules of product X formed per 100 eV absorbed by the total gas mixture and the component i , respectively.

All $G(N_2)_p$ values were derived from the $G(N_2)_t$ values applying correction for contribution of other components toward the nitrogen yield. $G(N_2)$ from N₂O was taken as 10.0 and for other components, when the contribution originated only from the produced electrons, $G(N_2) = 1/W = G_e$ was considered to be adequate. $G(H_2)_p$ values were corrected for the contribution of other hydrogen yielding components. Since the electron fractions of the components, other than propane,

were relatively low, the applied corrections were in all cases well below 10%.

C₃H₈ + N₂O (2 Mol %). Effect of Polar Molecules. The nitrogen yield in this system was greatly affected at 25° in the presence of polar molecules such as H₂O, NH₃, CH₃Cl, (CH₃)₂O. The results are presented in Figure 1 except for (CH₃)₂O since in this case it was difficult to determine quantitatively small amounts of CO in the presence of large quantity of N₂. The trend in the presence of (CH₃)₂O was similar to that shown in the presence of the other polar molecules; *i.e.*, $G(N_2)$ showed a tendency to decrease and approach G_e with increasing concentrations of (CH₃)₂O. The hydrogen yield was not affected by increased amount of additive, although it attained slightly different levels in the presence of different additives. $G(H_2)_p$ was 4.3 ± 0.2 , 4.8 ± 0.2 , 4.3 ± 0.2 , and 4.5 ± 0.2 , in the absence of an additive and in the presence of H₂O, NH₃, and CH₃Cl, respectively. The methane yield $G(CH_4) = 1.0 \pm 0.1$ was the same in all systems except in the presence of CH₃Cl where $G(CH_4) = 2.5 \pm 0.2$.

Effect of Temperature (Figure 2). In the absence of polar additives there is a sharp rise of $G(N_2)$ with increasing temperature reaching a plateau value of $2G_e$ at 80° and remaining constant up to 200°. Owing to the thermal radiolytic decomposition of C₃H₈ above 260°, the temperature was not raised much further. In the presence of 1 mol % of NH₃ the increase of $G(N_2)$ with temperature is considerably slower and $G(N_2)$ reaches the $2G_e$ value only at temperatures above 200°. In the presence of 7 mol % of water the increase in $G(N_2)$ is even more retarded and in the same temperature range $G(N_2)$ never reaches the $2G_e$ value. There is a slight in-

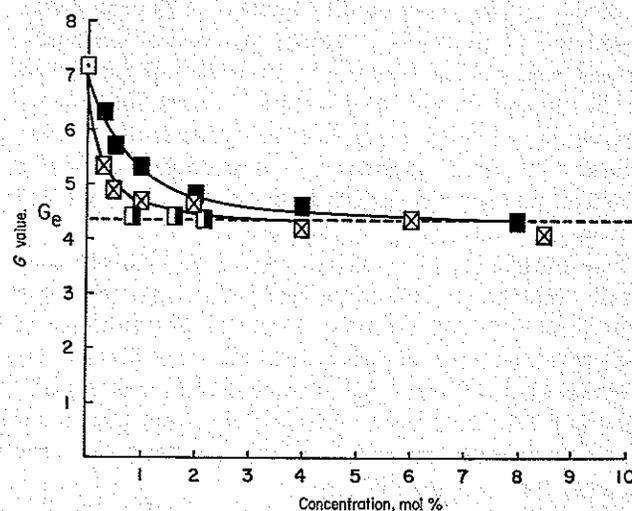


Figure 1. Nitrogen yields from the radiolysis of C₃H₈ + N₂O (2 mol %) at 25° in the absence of additives (□) and in the presence of: NH₃, ■; CH₃Cl, ⊠; H₂O, ■.

(8) F. T. Jones and T. S. Sworski, *J. Phys. Chem.*, **70**, 1546 (1966).

(9) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

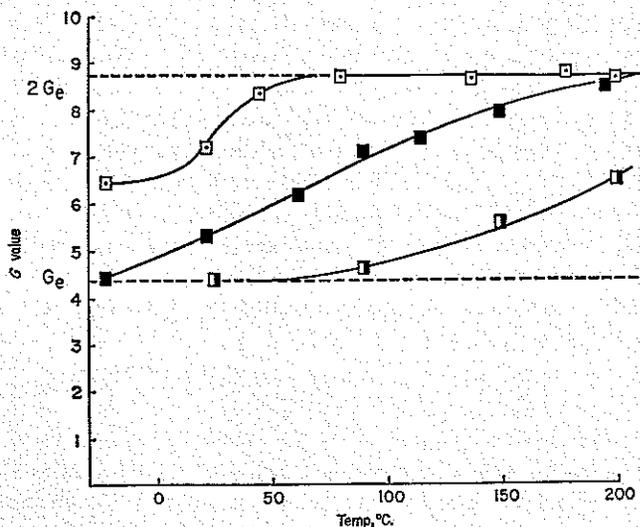


Figure 2. Effect of temperature on nitrogen yields from the radiolysis of C₃H₈ + N₂O (2 mol %) in the absence of additives (□) and in the presence of NH₃ (1 mol %), ■; H₂O (7 mol %), ▣.

crease in hydrogen yield in C₃H₈ + N₂O and C₃H₈ + N₂O + NH₃ mixtures reaching $G(\text{H}_2) = 4.9 \pm 0.2$, equivalent to the constant value of hydrogen observed in C₃H₈ + N₂O + H₂O. In all three cases $G(\text{CH}_4)$ rose from 1.0 to 3.4 at 200°.

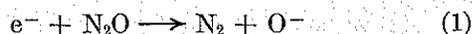
Cyclohexane + N₂O (2 Mol %). The nitrogen yield in this system was greatly reduced in the presence of H₂O although a greater concentration of H₂O was required owing to the higher temperature of the system. The results are presented in Table I. $G(\text{N}_2)$ approaches G_e only at the highest H₂O concentrations used.

Table I: Radiolysis of Cyclohexane + N₂O (2 mol %) + H₂O at 102°

H ₂ O, mol %	$G(\text{H}_2)_{\text{ch}}$	$G(\text{N}_2)_{\text{ch}}$
0	4.05	15.6
0.5	4.1	11.5
2.9	3.86	6.77
7.0	3.9	5.95
13	4.19	5.54
20	4.0	4.95

Discussion

The reaction of near-thermal or thermal electrons with N₂O in the gas phase has been observed both by mass spectrometric detection of O⁻ ions¹⁰ and in radiation chemistry¹¹ by measurement of N₂ yields. Until recently simple dissociative electron capture, as indicated by electron beam studies,¹⁰ has been assumed to occur in the radiolysis of systems containing N₂O.



More recently, evidence^{12,13} has been obtained that reaction of thermal electrons with N₂O at higher pressures is not a two-body dissociative capture. A pseudo-third-body reaction has been proposed at pressures 10-200 Torr



where M designates a third body; a three-body rate constant was also derived, $k_2 = 5.6 \times 10^{-33} \text{ cm}^4 \text{ sec}^{-1}$. A small amount of N₂O⁻ arising from reaction 3 has been actually detected in mass spectrometric experiments¹⁴ contradicting the arguments¹⁵ put forward against a possible formation of N₂O⁻. Further studies of the effect of temperature and pressure are obviously desirable.

To explain the mechanism of formation of the products in radiolysis of gaseous N₂O, secondary reactions were introduced¹⁶ (2.4 and 1 eV exothermic)

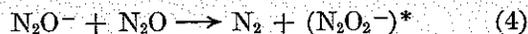


This reaction was also postulated¹⁷ in radiolysis of gaseous propane in the presence of small amount of N₂O (≤ 3 mol %). For a sufficiently high concentration of N₂O, depending on dose rate, all of the radiation produced electrons react with N₂O and the N₂ yield reaches a plateau value at $G(\text{N}_2) = 1.67G_e$.

On the basis of recent mass spectrometric evidence¹⁸ reaction 3c has to be taken into account



Assuming N₂O⁻, instead of O⁻, to be the species produced in the radiolysis at higher pressure (>10 Torr) as recently suggested¹² a reaction similar to reaction 3c could be introduced



The "excess N₂ yield," = $G(\text{N}_2) - G_e$, is formed then from further reactions or decomposition of (N₂O₂)^{*}.

Although we worked at relatively high pressures (≈ 1 atm) where third-body processes play a more prominent role, we shall for the time being consider the formation and possible reactions of both O⁻ and N₂O⁻.

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(14) J. F. Paulson, *Advances in Chemistry Series*, No. 58, American Chemical Society, Washington, D. C., 1966, p 28.

(15) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *J. Chem. Phys.*, **47**, 3085 (1967).

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The work discussed here is mainly concerned with the use of simple polar molecules with low electron affinities to cluster the precursor of the excess N_2 formed by processes other than reaction 1 or reaction 4. Although a complete mechanism for the formation N_2 cannot be given at present, it should be pointed out that two parts of the N_2 yield can be easily distinguished: (a) part equivalent to and originating from the radiation produced electrons—which can be reduced or eliminated by electron scavenger (*e.g.*, SF_6) and (b) excess N_2 yield—a secondary consequence of either reaction 1 or reaction 4.

Contrary to the radiolysis of $C_3H_8 + N_2O$ systems, where $G(N_2)/G_e = 1.67$, results from irradiated $D_2O + C_3H_8$ (1.5 mol %) + N_2O (3 mol %) at 140° indicate¹⁹ considerable suppression of reaction 3 or 4, *i.e.*, $G(N_2)/G_e = 1.06 \pm 0.1$. (This value is recalculated by using $G(N_2) = 10$ instead of 12 as used originally for the N_2O dosimeter.) This was attributed entirely to reaction of O^- with water. (N_2O^- can undergo the same reaction.)



It is an obvious conclusion that OD^- (or OH^- when H_2O is used) does not react with N_2O under these conditions. The same reaction was observed in mass spectrometric studies,²⁰ and it was concluded that both proton transfer and hydrogen atom abstraction contribute toward it. We shall see later that reaction 5 is not sufficient to explain the decrease in $G(N_2)/G_e$.

Studying the dependence of $G(N_2)/G_e$ on various additives in radiolysis of $C_3H_8 + N_2O$ (3 mol %) a series of chemical reactions of O^- was reported.^{21,22} In some cases $G(N_2)/G_e$ went down to 1 (CO_2 , propylene) and in some cases it went up to 2 (acetone) or even higher (alcohols). It was suggested that the reactions 3a and 3b could be both, or selectively, suppressed.

Some of the organic systems are not suitable for the study of the O^- reactions. For instance, in radiolysis of saturated alcohols,²³ cyclohexane (Table I), methylcyclohexane,²⁴ and benzene²³ in the presence of a small amount of N_2O (at about 100°) much higher values of $G(N_2)$ are obtained (15–40). No satisfactory explanation has been offered so far for those high $G(N_2)$ values. It is quite probable, though, that a short-chain mechanism is the main source of it involving either electron-transfer or free-radical reactions. We have been reluctant, therefore, to use any of these gases or additives that could lead to an extra not-well-specified yield of N_2 . Propane + N_2O appeared to be the most suitable system and by selecting relatively simple molecules our intention was to study their effect on reaction 3 or 4. Some of the otherwise suitable compounds such as CH_3Br and SO_2 could not be used because of their high electron reactivity.

The observed decrease of $G(N_2)/G_e$ to 1, in irradiated $C_3H_8 + N_2O$ (2 mol %) in the presence of sufficiently high concentration of these chosen polar additives (Fig-

ure 1), strongly suggests clustering of the ionic precursor of the extra N_2 yield whereby reaction 3 or 4 becomes endothermic. Assuming reaction 4 to become endothermic by clustering, the N_2 yield equivalent to G_e is then probably originating from either decomposition of the clustered N_2O^- or from its reaction with the positive ion. Whether the precursor of the extra N_2 yield is O^- or N_2O^- does not affect our conclusion since both of these ions are expected to form clusters.

The formation of clusters is a three-body process usually presented as



where P designates a polar molecule and M a third body. In our system all of the components present could act as third bodies, but their relative efficiencies are not known. At pressures above 1 Torr clustering is already very fast and efficient. At atmospheric pressures and the dose rate used, clustering is occurring before charge neutralization takes place.

Using a mass spectrometric technique Kebarle, *et al.*,³ have measured the heats of each particular clustering step and found the $-\Delta H$ for $H_3O^+ + H_2O$ is of the order 0.5–1.5 eV, being higher for the attachment of the first few H_2O molecules. It would not be unreasonable to assume similar values for O^- or N_2O^- and H_2O . Evidently reaction 3 or 4 would become endothermic after attachment of only a few H_2O molecules, since reaction 3a is 2.4 eV exothermic.

The clustering efficiency of a molecule is a function of its polarizability and polarity.²⁵ Higher clustering efficiency, and higher $-\Delta H$ for equivalent clustering steps, would determine the efficiency of the additive as a suppressor of reaction 3. Quantitative conclusions are difficult to reach because of the lack of pertinent data. It is of interest to note that CH_3Cl has a higher efficiency than NH_3 (Figure 1) in agreement with respective polarities (1.87 and 1.47 D). Some support for this observation is given by the recent observation^{4b} that Cl^- forms clusters with CCl_4 and $CHCl_3$ in irradiated $CCl_4 + CHCl_3$ mixtures. Their results show $CHCl_3$ to interact much more strongly with Cl^- than with CCl_4 and that this is due to the permanent dipole of this compound.

By increasing the temperature, declustering takes place and reaction 3 or 4 becomes more prominent. In $C_3H_8 + N_2O$ (2 mol %) + NH_3 (1 mol %) at 200° , all

(19) G. R. A. Johnson and M. Simic, *J. Phys. Chem.*, **71**, 1118 (1967).

(20) K. Jager, M. Simic, and A. Henglein, *Z. Naturforsch.*, **A**, **22**, 961 (1967).

(21) J. M. Warman, *J. Phys. Chem.*, **71**, 4066 (1967).

(22) J. M. Warman, *ibid.*, **72**, 52 (1968).

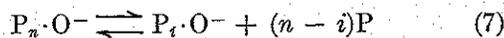
(23) M. Simic, unpublished results.

(24) W. J. Holtzlander and G. R. Freeman, *J. Phys. Chem.*, **71**, 2562 (1967).

(25) J. L. Magee and R. Funabashi, *Radiat. Res.*, **10**, 622 (1959).

O⁻ or N₂O⁻ ions have less than a critical number of NH₃ molecules attached. Reaction 3 or 4 becomes again exothermic; hence, $G(N_2) = 2G_e$ (Figure 2).

As we said above, there is a critical number of clustered molecules, i , separating the P _{n} ·O⁻ clusters into those undergoing reaction with N₂O ($n < i$) and the ones for which the same reaction becomes endothermic ($n > i$). An over-all equilibrium could be written that separates those two groups of clusters.



Relative equilibrium constants, K , at different temperatures for the above equilibrium could be calculated from Figure 2; $K = [G(N_2) - G_e]/[2G_e - G(N_2)]$. By plotting values of $\log K$ against $1/T$ one could calculate the energy required to convert the unreactive clusters into the reactive ones. The Arrhenius plots for both NH₃ and H₂O give relatively good linear fits yielding $\Delta E = 0.3$ eV (6.9 kcal/mol) and $\Delta E = 0.36$ eV (8.2 kcal/mol), respectively. This energy is related to $-\Delta H_{i,n}$ and more probably to $-\Delta H_{i,i+1}$. Both ΔE values fall into the expected range. More refined conclusions cannot be reached at present, and mass spectrometric data are therefore highly desirable.

In the presence of NH₃ and CH₃Cl, clustering of O⁻ or N₂O⁻ is probably the only process. No chemical reaction can be envisaged since proton-donating properties of NH₃ and CH₃Cl are very poor. Dehydrogenation of these molecules can also be ruled out since the bond energies of N-H in NH₃ (4.37 eV) and of C-H in CH₃Cl (4.08 eV) are higher than the bond energy of C-H in propane (3.97 eV). In addition, propane is present in a much higher concentration. Reaction of O⁻ + CH₃Cl → ClO⁻ + CH₃, similar to the reaction of O⁻ + CH₃I → IO⁻ + CH₃ observed in the mass spectrometer,²⁶ can be ruled out since CH₄ does not depend on N₂O/CH₃Cl ratio.

Proton donation is an additional process when H₂O or any other molecules with acidic properties are present, in agreement with previously reached conclusions.²⁰ Much higher efficiency of H₂O in suppressing reaction 3 or 4 is evident from Figure 1. The fact that $G(N_2)$ increases with temperature in C₃H₈ + N₂O (2 mol %) + H₂O (7 mol %) as well is a good indication that declustering contributes toward reaction 3 or 4, *i.e.*, that proton transfer is not the only process in the system.

In cyclohexane + N₂O + H₂O system (Table I), H₂O appears to be as efficient as in the above example. It is apparent that the clustering of O⁻ or N₂O⁻ inhibits the chain reaction where O⁻ or N₂O⁻ seems to be the precursor of the excess N₂ yield. It is less probable that H₂O would affect a neutral free-radical reaction with N₂O, and a neutral free-radical propagation step can be ruled out. The observed decrease of $G(N_2)/G_e$ in irradiated C₃H₈ + N₂O + C₃H₆ system could be explained by addition of O⁻ to the double bond as suggested previously.²¹ On the other hand, it is also possible that

the effect is partly or entirely due to the clustering of O⁻ or N₂O⁻ by propylene (0.35 D). The existing experimental results are insufficient to discriminate between those two processes. The question also remains about the importance of clustering of the negative ions in the radiolysis of N₂O (0.14 D).

We would like to point out that the ion-molecule and ion-ion reactions are not truly homogeneous reactions at pressures in the region of 1 atm because of the interaction of ions with the induced or permanent dipoles. In fact, in the presence of molecules with strong permanent dipoles, the situation microscopically might resemble the conditions in the liquid phase. A comparison of our systems with the corresponding liquid ones seems, therefore, to be pertinent. In aqueous solutions of N₂O, it is generally accepted that $G(N_2)/G_e = 1.00$. The reaction of O⁻ with N₂O is stopped completely by fast solvation of the ion. In liquid ammonia solutions of N₂O, such comparison cannot be made since NH₃ appears to react with N₂O.^{27,28} Such a reaction under our conditions should not be taken into consideration partly due to a small production of NH₂ and partly because of preferential reaction of NH₂ with propane.²⁸

The observation of a temperature dependence of $G(N_2)$ in C₃H₈ + N₂O (2 mol %) is very interesting. The fractional ratio of $G(N_2)/G_e = 1.67$ disappears and becomes 2 at temperatures above 80°. It is possible that a small amount of H₂O, which cannot be pumped out, is always present on the walls of the vessels, and that introduction of other gases desorbs it. Whether these minute amounts could affect reaction 3 or 4 is not clear. An extremely high clustering rate for O₂⁻ with H₂O, *i.e.*, $>10^{-28}$ cm⁶ sec⁻¹, was reported.²⁹ The high efficiency of this process is illustrated by the fact that they observed (H₂O)₂·O₂⁻ at pressures as low as 10⁻⁴ Torr. Kebarle, *et al.*,^{4a} have also observed the existence of (H₂O)·O₂⁻ in the O₂-H₂O mixtures in the gas phase. The O₂⁻ and O⁻ ions carried one or two H₂O molecules even when supposedly completely dry O₂ was used. On the other hand, one could assume a change of reaction mechanism with temperature. Whatever the reason for the increase in $G(N_2)$ with temperature, it would be convenient in many cases to replace the unknown reaction mechanism with a stoichiometric relationship at temperatures not much above room temperature (>80°).

N₂O has been suggested¹⁷ as a suitable reference compound for studying relative rates of electron attachment, partly due to its highly specific reactivity and

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(28) G. R. A. Johnson and M. Simic, *Advances in Chemistry Series*, No. 82, American Chemical Society, Washington, D. C., 1968, p 197.

(29) J. L. Moruzzi and A. V. Phelps, *J. Chem. Phys.*, **45**, 4617 (1966).

partly because of its unreactive and easily measured product. It is obvious, although not always recognized, that $k(e + N_2O)/k(e + S)$ cannot be worked out from a decrease in $G(N_2)$ if reaction 3 or 4 is affected by clustering proton transfer or any other similar reaction.

The hydrogen and methane values agree reasonably well with the previously reached conclusions.¹⁷ A relatively small effect of additives and temperature on

$G(H_2)$ does not present a significant difference. The increase of $G(CH_4)$ with temperature is probably due to enhanced fragmentation at higher temperatures. No explanation is offered for the high value of $G(CH_4)$ in $C_3H_8 + N_2O + CH_3Cl$ at room temperature.

Acknowledgment. We are grateful to Professor J. J. Weiss for encouragement and Dr. G. R. A. Johnson for many stimulating discussions.