J. Phys. Chem. A **2000,** *104,* 67−71

Thermal Electron Capture in the Mixtures of Halocarbons and Environmental Gases

Andrzej Rosa and Iwona Szamrej*

Chemistry Department, University of Podlasie, Siedlce, Poland

Received: July 20, 1999; In Final Form: October 20, 1999

The electron capture processes in the mixtures containing halocarbons (CHF_3 or $CClF_3$) and nitrogen have been investigated. Second- and third-order kinetics were observed in both cases. The electron interaction with van der Waals complexes $CHF_3{\cdot}N_2$ and $CClF_3{\cdot}N_2$ was invoked to explain this behavior and the corresponding rate constants have been determined. The values for two-body processes (5×10^{-14} cm^3 molecule^{-1} s^{-1} −CHF_3 and 1.3×10^{-13} cm^3 molecule^{-1} s^{-1} −$CClF_3$) are fully consistent with the literature data. The estimated rate constants for electron capture by van der Waals complexes are equal to 1.2×10^{-10} and 2.4×10^{-11} cm^3 molecule^{-1} s^{-1} for $CHF_3{\cdot}N_2$ and $CClF_3{\cdot}N_2$, respectively.

Introduction

Electron attachment processes in the gas phase have been studied extensively within the past three decades.[1−3] They can be broadly divided into two groups: two-body processes occurring under single collision conditions and the multibody pressure-dependent ones. If both of them occur with comparable rates they can be observed in the high-pressure (around atmospheric and higher) experiments, e.g., swarm or pulse radiolysis.[2−5]

The electron collision with individual molecule (AB) leads to an excited negative ion state (reaction 1) which can either autoionize (reaction 2) or give attachment products: parent negative ion or dissociation fragments.[1]

$$e + AB \rightarrow AB^{-*} \qquad (1)$$

$$AB^{-*} \rightarrow AB + e \qquad (2)$$

$$AB^{-*} \rightarrow AB^{-}\{\text{or } A + B^{-}\} \qquad (3)$$

If the lifetime of AB^{-*} is long enough ($>10^{-11}$ s) and the concentration of the environmental gas, M_s (it could be also AB), is sufficient then the excited negative ion can be collisionally stabilized (reaction 4). The entire attachment process is then pressure dependent and kinetically is of the third order.[4,5]

$$AB^{-*} + M_s \rightarrow \text{products} \qquad (4)$$

Such a mechanism is called collisionally stabilized attachment or Bloch−Bradbury (BB) mechanism. In this case, the rate of the electron disappearance is described by eq 5

$$v = \frac{-d[e]}{dt} = \frac{k_1 k_4 [AB][M_s]}{k_2 + k_4[M_s]} \qquad (5)$$

However, there are a lot of cases where the third-order kinetics cannot be explained by the BB mechanism. The only explanation that can be then applied is that electrons are accepted not by individual molecules but by van der Waals (vdW) complexes preexisting in all gaseous mixtures.[6−16] In this case the mechanism of the process is exactly the same as for single molecule and the concentration of the vdW complex is defined by the equilibrium constant of its formation (reaction 6).

$$AB + M \rightleftharpoons (AB{\cdot}M) \qquad (6)$$

$$e + (AB{\cdot}M) \rightarrow (AB{\cdot}M)^{-*} \qquad (7)$$

$$(AB{\cdot}M)^{-*} \rightarrow AB + M + e \qquad (8)$$

$$(AB{\cdot}M)^{-*} \rightarrow \text{products} \qquad (9)$$

$$(AB{\cdot}M)^{-*} + M_s \rightarrow \text{products} \qquad (10)$$

where M denotes AB (homogeneous complex) or any other molecule (heterogeneous).

This type of the behavior is called van der Waals mechanism. The kinetic eq 11 shows the straightforward dependence of the rate of the process on the product of component concentration if the process goes through reactions 6−9.

$$v = \frac{-d[e]}{dt} = \frac{k_7 k_9 K_{eq}[AB][M]}{k_8} \qquad (11)$$

If reaction 10 replaces reaction 9, then eq 12 describes the kinetics

$$v = \frac{-d[e]}{dt} = \frac{k_7 k_{10} K_{eq}[AB][M][M_s]}{k_8 + k_{10}[M_s]} \qquad (12)$$

and the collisionally stabilized process with vdW complex instead of individual molecule takes place.

There is no straightforward way to measure the concentration of the vdW complex but the method developed by Stogryn and Hirschfelder[17] based on using second virial coefficient is usually applied.[6−15,18−20] The calculated equilibrium constants, K_{eq}, are mostly in the range of 10^{-21}−10^{-22} cm^3 molecule^{-1}. The ratio of the equilibrium concentration of the vdW complex to that of electron acceptor is equal to

$$[AB{\cdot}M]/[AB] = K_{eq}[M] \qquad (13)$$

Using calculated values of K_{eq}, one can estimate this ratio which for, e.g., 1 atm of M is equal to ca. 0.01. This is surprisingly high concentration which is not always recognized.

10.1021/jp992475m CCC: $19.00

If the kinetics of the electron attachment is formally of the third order, it is usually very difficult to decide which mechanism takes place unless at the high concentration of the third body, M_s, the point where collisional stabilization is faster than autoionization ($k_4[M_s] \gg k_2$), is reached. Then the so-called "saturation effect" is experimentally visible (the rate of the process starts to be independent of $[M_s]$) and one can be sure that the process goes accordingly with the BB mechanism. If this condition is not fulfilled then it is not possible to distinguish which mechanism really occurs from the kinetic data. If in the whole concentration range the linear dependence of the rate of the process on $[M_s]$ is observed then either $k_2 \gg k_4[M_s]$ or the attachment involves vdW molecules (RX•M). The concentration of the complex increases with M. The situation is much simpler if one deals with formally fourth-order kinetics. Then the first step should be the electron capture by vdW molecule and the second one the BB stabilization.

In our recent papers,[18−20] we have investigated thermal electron capture processes in the mixtures of some halomethanes diluted with carbon dioxide. We have found that except for the rather slow second-order reaction (single collision)

$$e + RX \rightarrow \text{products} \qquad (14)$$

where the preferred channel is the dissociation with formation of the negative halogen ion, other processes occur which involve either homo- $(RX)_2$ or heterogeneous $(RX{\cdot}CO_2)$ van der Waals complexes (multibody pressure dependent processes) and are at least a couple of times faster at atmospheric pressures

$$e + (RX)_2\,\{\text{or } (RX{\cdot}CO_2)\} \rightarrow \text{products} \qquad (15)$$

or

$$e + (RX)_2\,\{\text{or } (RX{\cdot}CO_2)\} + M_s \rightarrow \text{products} \qquad (16)$$

where M_s = RX and CO_2.

It is extremely urgent to develop methods for removing Freons from the air. Among the various possible ways suggested for destroying halocarbons there are several plasma methods: by an electron beam or by using a free localized microwave discharges.[21,22] The key processes in these studies are electron attachment reactions. For modeling the system it is necessary to know the exact rate constants of these processes, and their mechanism and products.

The purpose of this work was to reveal the mechanism and the kinetics of the electron attachment in the mixture of some halomethanes and nitrogen.

Experimental Section

The electron swarm experiment with ionization chamber, as introduced by Christophorou,[1] is one of the important techniques in studying the electron attachment processes. However, for the investigations of the electron attachment mechanism this technique has to be modified to allow the measurements with different environmental gases.[24] Such modification allows the measurements only with electrons in thermal equilibrium. But if one wants to investigate the processes occurring in the lower atmosphere he deals with low energy electrons. Also, the processes involving more than one isolated molecule usually occur with thermal energy electrons.

The modified electron swarm method used in the experiment has been fully described elsewhere.[23] Briefly, it consists of monitoring the rate of electron disappearance from the swarm as a function of the density reduced electric field, E/N. Electrons are produced by collimated α-source (^{238}Pu isotope). The measured quantity is the electron attachment coefficient, α, which is the probability of electron attachment per unit density of the attaching gas (cm^2 molecule^{-1}). To get the rate constant for the attaching process, k_α, the attachment coefficient has to be multiplied by the electron swarm drift velocity, W. If one keeps E/N low enough, the electron swarm attains thermal energy distribution and k_α has its classical meaning. Usually CO_2 is used as the carrier gas as it is a very good thermalizing agent providing electrons with energy in thermal equilibrium. In this work, nitrogen was used. It has a very narrow range of E/N values where electrons are fully thermalized. Its concentrations varied from 1×10^{19} to 3.3×10^{19} molecules cm^{-3} (300−1000 Torr) so the applied electric field where electrons reach thermal equilibrium could be only up to 40 V ($E/N < 6 \times 10^{-19}$ V cm^2 molecule^{-1}). However, in all experiments the concentration of the admixture (halomethanes) was high enough to have a great influence on the thermalization process. The concentration of both halomethanes used varied from about 0.3×10^{18} up to 2×10^{18} molecules cm^{-3} and the percentage of the admixture was in the range of 3−6%. So, the applied electric field can be higher than that in pure nitrogen and electrons are still in thermal equilibrium. We have used the E/N values up to 3×10^{-17} V cm^2 molecule^{-1}.

The drift velocity of electrons depends on the concentration of additives in the carrier gas.[24] In a study of processes in which the amounts of additives should be high, as in the case of higher than second-order kinetics, one must find a way to get the electron drift velocity in a particular mixture. For electrons with thermal energy distribution it is possible if one uses, e.g., SF_6 as a probe.[23] This, however, may be confusing, especially in multicomponent systems where the biggest experimental error is made in the precise determining the concentration.

Taking into account that electron drift velocity for electrons in a thermal equilibrium with gas molecules is a linear function of E/N [25]

$$W = \mu_N E/N \qquad (17)$$

where μ_N is a density normalized electron mobility expressed in V^{-1} cm^{-1} s^{-1}, one can get[24]

$$V_{\max} = f(E/N)_{k_\alpha,\mu_N} \qquad (18)$$

where $V_{\max}$ is the amplitude of the electron pulse which is registered in the multichannel analyzer. The values of k_α and μ_N can be found with a fitting procedure especially when the experiment is performed in series with constant μ_N, i.e., at constant molar ratio of the components (as μ_N does not depend on the overall pressure). Such an approach allows one to investigate thermal electron capture processes in different gaseous mixtures to get the kinetics and in particular to look for the influence of the environmental gases on the attachment mechanism. This method has been fully described in our previous papers where we have measured also the thermal electron mobilities in no electron attaching mixtures containing nitrogen and some noble gases.[24] The results we have got are in perfect agreement with the ones obtained using other methods.

Recently, we have developed the new procedure[26] which allows to establish independently electron mobility or electron drift velocity in any mixture and for different electron energy distribution. It is based on the analysis of the time evolution of the electric pulse registered on the oscilloscope with digital memory. This new method gives results fully consistent with

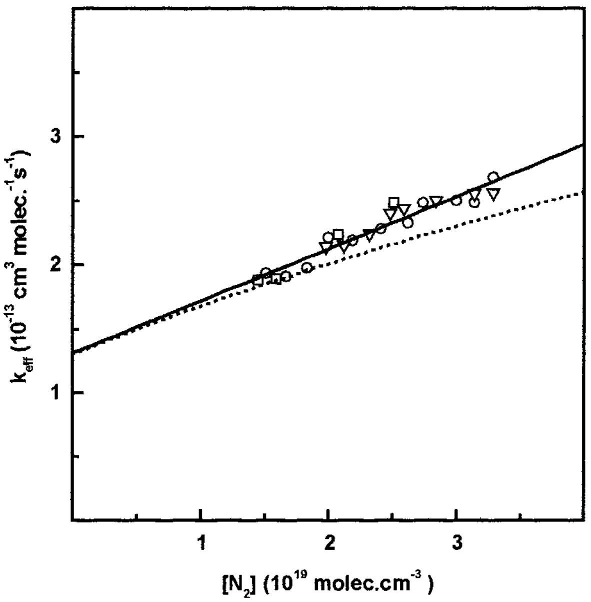

Figure 1. Influence of nitrogen concentration on k_{eff} obtained in the mixture of $CClF_3$−N_2: $[CClF_3]/[N_2]$ = (□) 0.041, (▽) 0.030, (○) 0.025. For the meaning of the dotted line see text.

the calculations we usually use. The accuracy for both methods is better than 5%.

All the measurements were carried out at the room temperature (293 K). The total rate of the process was kept at around 10^5 s^{-1}.

Results and Discussion

Electron attachment processes by CHF_3 and $CClF_3$, diluted with nitrogen, have been investigated. The rate of electron disappearance from the swarm has been measured. The results are presented in terms of k_{eff}, which is the rate constant for the hypothetical two-body process

$$e + RX \xrightarrow{k_{eff}} \text{products} \qquad (19)$$

otherwise, the rate of electron disappearance divided by admixture concentration, [RX].

In Figure 1 k_{eff} vs $[N_2]$ for $CClF_3$−N_2 mixture is plotted. The experiments were performed for different molar ratios of $[CClF_3]/[N_2]$ from 0.025 to 0.041.

In Figure 2 the results for the CHF_3−N_2 mixture are plotted in the same coordinates as above. The experiment was performed for three molar ratios of $[CHF_3]/[N_2]$ = 0.040, 0.044, and 0.063.

The nonzero intercept which is seen in both figures means that there is a reaction whose rate depends only on electron and halomethane concentration. This is similar to the results we have got in the previous studies[18−20] where we investigated the mechanism and the kinetics of the electron capture processes with the same halomethanes as in this work but in the presence of carbon dioxide. We have found that in all cases other pressure-dependent processes of electron attachment also take place.

The common feature for both systems investigated here is the two-body process

$$e + RX \rightarrow RX^- \{\text{or } R + X^-\} \qquad (20)$$

occurring with a small rate constant of 10^{-13}−10^{-14} cm^3 molecule^{-1} s^{-1}.

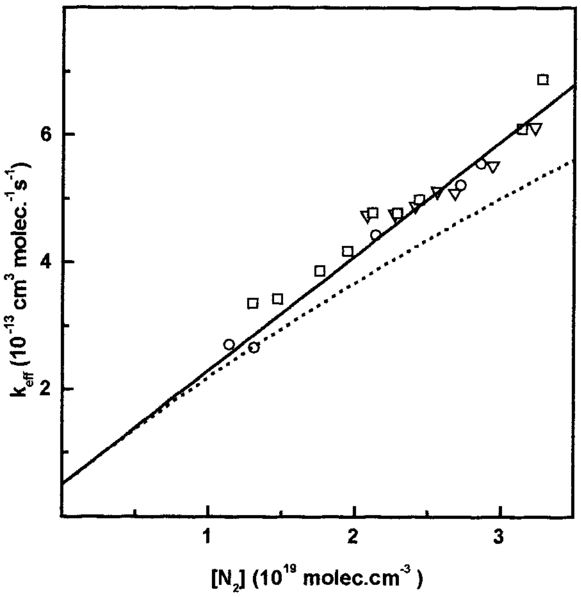

Figure 2. Influence of nitrogen concentration on k_{eff} obtained in the mixture of CHF_3−N_2: $[CHF_3]/[N_2]$ = (○) 0.063, (▽) 0.044, (□) 0.040. For the meaning of dotted line see text.

TABLE 1: Two-Body Thermal Electron Attachment Rate Constants ($k_{two-body}$, in cm^3 molecule^{-1} s^{-1})

RX molecule	present data with N_2	previous data[19] with CO_2	literature data[a]
CHF_3	5×10^{-14}	2.2×10^{-14}	3.6×10^{-14}, 4.6×10^{-14}, $<6.2 \times 10^{-14}$
$CClF_3$	1.3×10^{-13}	1.0×10^{-13}	5.2×10^{-14}, 7×10^{-14}, 2×10^{-13}, $<3.1 \times 10^{-13}$

[a] References as in ref 3.

TABLE 2: Thermal Electron Attachment Rate Constants by vdW Complexes (k_{vdW})

complex	k_{exptl} (cm^6 molecule^{-2} s^{-1})	K_{eq} (cm^3 molecule^{-1})	k_{vdW} (cm^3 molecule^{-1} s^{-1})
$CHF_3 \cdot N_2$	1.8×10^{-32}	1.45×10^{-22}	1.2×10^{-10}
$CClF_3 \cdot N_2$	4.0×10^{-33}	1.67×10^{-22}	2.4×10^{-11}

These rate constants are presented in Table 1 together with the previous values (from the experiments with CO_2) and the literature data. As one can see, there is very good agreement between these two experiments especially if one takes into account that the constants are very small.

In both the mixtures investigated in the present study we observe the linear dependence of k_{eff} on nitrogen concentration. This shows that we deal also with summarily third-order processes whose rates depend also on the nitrogen concentration. The three-body collisionally stabilized electron attachment (the BB mechanism) has to be excluded. As seen from both figures, k_{eff} depends only on nitrogen concentration. If the excited negative ion, RX^{-*}, was stabilized in collision, the influence of [RX] on the stabilization rate had to be clearly visible due to much higher stabilization efficiency of halocarbon than that of nitrogen (about 100 times).[4] Halomethanes densities were only 1−2 orders of magnitude lower than the ones for nitrogen. So k_{eff} should depend on $[N_2]$ + 100[RX] and this is not the case. Also, the comparison of the present results with the ones obtained in the mixtures of halocarbons and carbon dioxide allows excluding Bloch−Bradbury mechanism.

In the mixture of $CClF_3$ with CO_2, exactly the same dependence as for the system with N_2 has been observed. That is, k_{eff} depended linearly on $[CO_2]$ and the mechanism of the process involved ($CClF_3 \cdot CO_2$) complexes as we have proved comparing the possible lifetime of the $CClF_3^{-*}$ ion with collision frequency.[18]

The collision frequency as calculated from the Langevin equation is equal to ca. 7×10^{-10} cm^3 molecule^{-1} s^{-1}. It does not differ much if CO_2 is replaced by N_2. Also, the experimental value obtained by Hatano[16] for the system O_2-CO_2 is equal to ca. 6×10^{-10} s^{-1}. So the calculations seem reasonable. With that, the rate of stabilization for both carbon dioxide and nitrogen as the stabilizing agents for the highest used concentrations $[M_s]_{max} = 3.3 \times 10^{19}$ molecules cm^{-3} is equal to about 2.3×10^{10} s^{-1}. Now, taking into account the results presented in Figures 1 and 2, one can estimate the highest possible lifetime of the negative ions. Even at rather weak conditions estimated for the BB mechanism

$$e + CClF_3 \xrightarrow{k_{21}} CClF_3^{-*} \tag{21}$$

$$CClF_3^{-*} \xrightarrow{k_{22}} e + CClF_3 \tag{22}$$

$$CClF_3^{-*} + N_2 \xrightarrow{k_{23}} \text{products} \tag{23}$$

$k_{23}[M]/k_{22} = >0.05$ which corresponds to the autodetachment lifetime of the excited negative ion $\tau = 1/k_{22} = < 2 \times 10^{-12}$ s the deviation from linearity has to be observed. The dotted lines in both figures calculated using the above conditions show that this is not the case. Even at our scattering of the experimental points we do not observe the deviation from the linearity expected in BB mechanism.

So, we can claim that in this case electrons are accepted by the complex ($CClF_3 \cdot N_2$). The rate constant for this process (reaction 24) estimated from the slope of the line in Figure 1 and respective K_{eq} (1.67×10^{-22} cm^3 molecule^{-1}) is equal to 2.4×10^{-11} cm^3 molecule^{-1} s^{-1}.

$$e + (CClF_3 \cdot N_2) \xrightarrow{k_{24}} \text{products} \tag{24}$$

A more complicated situation is in the CHF_3-N_2 mixture. Previous results showed that in the CHF_3-CO_2 system the electron attachment process was formally of the fourth order and the rate of electron disappearance depended on [CHF_3], [CO_2], and a summary concentration of both components, so the k_{eff} was a function of a product ([CHF_3] + [CO_2])[CO_2].[19] This behavior could only be explained in terms of both vdW and Bloch−Bradbury mechanisms where the attaching individual was vdW complex ($CHF_3 \cdot CO_2$).

$$e + (CHF_3 \cdot CO_2) \rightarrow (CHF_3 \cdot CO_2)^{-*} \tag{25}$$

The collisional stabilization (27) competed with the process of autoionization of the excited negative ion (26).

$$(CHF_3 \cdot CO_2)^{-*} \rightarrow CHF_3 + CO_2 + e \tag{26}$$

$$(CHF_3 \cdot CO_2)^{-*} + M_s \rightarrow \text{products} \tag{27}$$

In this work, in the mixture of CHF_3-N_2 there is only straight linear dependence of k_{eff} on [N_2] in the whole region of the component concentrations used. So the attachment process goes through ($CHF_3 \cdot N_2$) complexes and the excited negative ion formed in reaction 28 is not collisionally stabilized.

$$e + (CHF_3 \cdot N_2) \rightarrow (CHF_3 \cdot N_2)^{-*} \tag{28}$$

It means that its lifetime is much shorter than that of the ion produced in reaction 25 which we have estimated as $>5 \times 10^{-11}$ s, so it can either autoionize in reaction 29 or immediately dissociate into the attachment products, reaction 30.

$$(CHF_3 \cdot N_2)^{-*} \rightarrow CHF_3 + N_2 + e \tag{29}$$

$$(CHF_3 \cdot N_2)^{-*} \rightarrow \text{products} \tag{30}$$

The rate constant for this process experimentally obtained from the slope of the line in Figure 2 is equal to 1.37×10^{-32} cm^6 molecule^{-2} s^{-1}. Applying the respective K_{eq} (1.45×10^{-22} cm^3 molecule^{-1}), we obtain electron attachment rate constant to ($CHF_3 \cdot N_2$) complex equal to 2.4×10^{-11} cm^3 molecule^{-1} s^{-1}.

We have observed the influence of the second component of the mixture on the mechanism of the process also in the case of CH_2F_2.[19] While in the $CH_2F_2-CO_2$ system the attachment goes through $(CH_2F_2)_2$ complexes, this process is not visible in $CH_2F_2-N_2$ where only the two-body reaction with a very small contribution of ($CH_2F_2 \cdot N_2$) is observed. It seems that the environmental gas has a strong influence both on the equilibrium constant of the vdW complex formation as well as on the lifetime of the complex negative ion.

The results presented in this paper fully support our latest conclusions[27] about the mechanism of vdW interaction on electron capture process. In the case of halocarbons, electron capture occurs by filling the same orbital both in an isolated molecule and in the vdW complex. The increase in k_{vdW} in comparison with $k_{two-body}$ is caused by shifting the potential curve of the negative ion state by intermolecular interaction in the vdW complex in such a way that it decreases the activation energy and increases the Boltzman factor, $e^{-E_a/kT}$, in the Arrhenius equation for the process. If we assume that the changes in the preexponential factor of this equation can be neglected, then the corresponding ΔE_a required for causing the observed increase in the rate constant is given by

$$\Delta E_a = kT \ln(k_{vdW}/k_{two-body}) \tag{31}$$

The value of ΔE_a is about 5 and 8 kT for $CClF_3$ and CHF_3, respectively. This can be compared with the energy of vdW interaction. ΔE_a can be even slightly lower if we also take into account that the preexponential factor can increase in the vdW complex as two molecules are available. All this leads to the final statement that the potential curve for the complex ion is shifted to lower energies as compared with the isolated ion and the crossing point with neutral molecule also moves toward lower energies. Qualitatively, it is rather obvious. But there are also quantitative results of McFadden et al.[28] supporting this statement. They calculated changes in the structure of some halocarbons due to electron attachment and have found that the main effect is an increase in the equilibrium length of the carbon−halogen bond corresponding to the reaction coordinate. They have compared the relative increase in these lengths with the corresponding rate constants for the two-body thermal electron attachment at the room temperature. From this comparison it is clearly seen that the higher the change in the bond length the lower the rate constant and so the effect is caused by changes in activation energy. This fully supports our conclusions.

Conclusions

We have proved that CHF_3 and $CClF_3$ in the mixture with nitrogen accept electrons in two ways: as individual molecules and van der Waals complexes. The formation of vdW bond lowers substantially the activation energy of the process, increasing greatly the rate constant in comparison with the isolated molecule. The equilibrium constant and the lifetime of the negative ion depend very strongly on the nature of the second component of the vdW complex.

References and Notes

(1) Christophorou, L. G. *Atomic and Molecular Radiation Physics*; Wiley-Interscience: New York, 1971.

(2) Hatano, Y.; Shimamori, H. *Electron and Ion Swarm*; Pergamon Press: New York, 1981; Chapter 2.

(3) McCorkle, D. L.; Christodoulides, A. A.; Christophorou, L. G. *Electron Molecule Interaction and their Applications*; Academic Press: New York, 1984; Chapter 6, Vol. 1

(4) Hatano, Y. *Electronic and Atomic Collisions*; Elsevier Science: Amsterdam, 1986; p 153.

(5) Armstrong, D. A. *Radiation Chemistry: Principals and Applications*; VCH: Weinheim, Germany, 1987; Chapter 9.

(6) Armstrong, D. A.; Nagra, S. S. *J. Phys. Chem*. **1975**, *79*, 2875.

(7) Nagra, S. S.; Armstrong, D. A. *Can. J. Chem.* **1975**, *53*, 3305.

(8) Nagra, S. S.; Armstrong, D. A. *Can. J. Chem*. **1976**, *54*, 3580.

(9) Nagra, S. S.; Armstrong, D. A. *J. Phys. Chem*. **1977**, *81*, 599.

(10) Nagra, S. S.; Armstrong, D. A. *Radiat. Phys. Chem*. **1978**, *11*, 305.

(11) Shimamori, H.; Fessenden, R. W. *J. Chem. Phys*. **1979**, *71*, 3009.

(12) Shimamori, H.; Hotta, H. *J. Chem. Phys*. **1988**, *89*, 2938.

(13) Shimamori, H.; Hotta, H. *J. Chem. Phys*. **1989**, *90*, 232.

(14) Toriumi, M.; Hatano, Y. *J. Chem. Phys*. **1983**, *79*, 3749.

(15) Toriumi, M.; Hatano, Y. *J. Chem. Phys*. **1984**, *81*, 3748.

(16) Hatano, Y. *Pulse Radiolysis*; CRC Press: Boca Raton, FL, 1991; Chapter 9.

(17) Stogryn, D. E.; Hirschfelder, J. O. *J. Chem. Phys*. **1959**, *31*, 1531.

(18) Szamrej, I.; Tchórzewska, W.; Kość, H.; Foryś, M. *Radiat. Phys. Chem*. **1996**, *47*, 269.

(19) Szamrej, I.; Kość, H.; Foryś, M. *Radiat. Phys. Chem*. **1996**, *48*, 69.

(20) Szamrej, I.; Jówko, J.; Foryś, M. *Radiat. Phys. Chem*. **1996**, *48*, 65.

(21) Aleksandrov, N. L.; Vakhrameev, K. V.; Dobkin, S. V.; Son, E. E. *Sov. Technol. Phys. Lett*. **1992**, *18*, 91.

(22) Aleksandrov, N. L.; Dobkin, S. V.; Konchakov, A. N.; Novitskii, D. A. *Plasma Phys. Rep*. **1994**, *20*, 442.

(23) Szamrej, I.; Foryś, M. *Radiat. Phys. Chem*. **1989**, *33*, 393.

(24) Dmitriev, O. W.; Tchórzewska, W.; Szamrej, I.; Foryś, M. *Radiat. Phys. Chem*. **1992**, *40*, 547.

(25) Gee, N.; Freeman, G. R. *J. Chem. Phys*. **1984**, *81*, 3194.

(26) Rosa, A.; Foryś, M.; Szamrej, I. *Gaseous Dielectrics VII*; Kluwer Academic/Plenum Publishers: New York, 1998; p 69.

(27) Szamrej, I.; Foryś, M. *Prog. React. Kinet*. **1998**, *23*, 117.

(28) Burns, S. J.; Matthews, J. M.; McFadden, D. L. *J. Chem. Phys*. **1996**, *100*, 1943.