# Dissociation of Propylene Excited by the Impact of Low-Energy Electrons in the Gas Phase

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Dissociation of gaseous propylene excited by the impact of low-energy electrons was investigated by using tritium  $\beta$ -rays in the presence of applied electric fields. The yields of  $C_1$ - $C_6$  hydrocarbon products are reported depending on the applied potential. To achieve a material balance for the free-radical processes, we performed the experiments at a temperature of 195 K. Decomposition of propylene excited by the electrons having energy below the ionization potential involves mainly either C-H (yielding  $H + C_3H_5$ ) or C-C (yielding  $C_2H_3 + CH_3$ ) bond rupture. The contribution of the latter increases with increasing electron energy. The experimental results agree quite well with RRKM calculations concerning vibrationally excited propylene molecules in the ground state. In radiolysis in the absence of electric fields the excited molecules appear to have energies higher than, or close to, the ionization threshold.

### Introduction

Although the reactions of excited molecules are acknowledged to be of great importance in radiation chemistry of hydrocarbons, the details of a mechanism for dissociation of excited propylene molecules are not indisputable. The results obtained so far differ among themselves depending on the manner of excitation and the experimental techniques used. Direct photolysis over the range of energies 6.7-10 eV<sup>1</sup> as well as mercury-sensitized photolysis<sup>2</sup> result in a cleavage of the C–H and C–C bonds; the former process is reported to predominate. This observation is confirmed by Rabinovitch et al. in the experiments on the dissociation of chemically activated propylene formed in reaction of methylene radical with ethylene.<sup>3a</sup> On the other hand, vibrationally excited propylene formed as an intermediate in photolysis of diazo-*n*-propane undergoes mainly the  $\hat{C}$ -C scission according to Figuera et al.<sup>3b</sup> Derai and Danon,<sup>4</sup> in the lowenergy (3.5-15 eV) electron-impact study of propylene  $(10^{-2})$ torr), the so called "simulated radiolysis", established that the triplet state at  $\sim$ 4.4 eV undergoes the cleavage of the C-C bonds predominantly; the contribution of the C-H bond rupture increases with increasing electron energy. The probability that at low pressures used the reactive intermediates will diffuse to the walls of a reaction vessel and react there is an obvious disadvantage of the method. Butkovskaya et al.<sup>5</sup> also suggest that decomposition of propylene excited by the impact of low-energy electrons (E < 7 eV) involves C–C breakage predominantly; unfortunately these authors give no convincing arguments to support this statement.

Some clues as to those products which are formed as a result of the excitation of the parent molecule can be

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gained from examination of the product yields under conditions when electric fields are applied during radiolysis. This old technique,<sup>6</sup> now obsolete, was helpful in elucidating some features of a mechanism of 1-butene radiolysis.<sup>7</sup> It is used in the present work to establish the reaction channels for the propylene excited in collisions with slow electrons (E < IP) and to check whether the simulated radiolysis of Danon can provide an estimate for the events occurring at pressures applied in conventional radiolytic studies.

# **Experimental Section**

Propylene (Fluka puriss. grade) was purified by gas chromatography until it contained no other hydrocarbon impurities than a few tenths ppm of propane.

Irradiation cells were glass cylinders with volumes of  $\sim$  60 mL, fitted with two parallel plate electrodes at each end. One of the electrodes of the ionization chamber was equipped with a titanium tritide source with an activity of 3 Ci. The plates were separated by a distance of 20 mm. Cells were fitted with a grease-free stopcock for attachment to a high-vacuum sampling system or to a gas chromatograph. The irradiations were carried out at a temperature of 195 K (dry ice-acetone slush) at a constant pressure of 32 torr. Some experiments were made at room temperature.

A stable saturation current of  $I = 6.5 \times 10^{-8}$  A extends over a plateau region beginning at 500 V and ending at 2400 V. The dose rate in the absence of the field is 9.9  $\times 10^{12} \text{ eV s}^{-1}$  based on  $W(C_3H_6) = 24.8 \text{ eV}.^8$  The main experiments covered the region 1300–2600 V (E/p varied from 20.3 to 40.6 V cm<sup>-1</sup> torr<sup>-1</sup>).

### Results

The yields of the different hydrocarbons formed in  $\beta$ radiolysis are assembled in Table I and are plotted against potential between the electrodes in Figure 1. The values are expressed in M/N units; dosimetry was based on the measurements of ionization current during radiolysis. The yields were obtained at 195 K, but for comparison the

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TABLE I: Dependence of the Product Yields on Potential Applied to the Electrodes in  $\beta$  Radiolysis at a Temperature of 195 K

potential (V) saturation current, 10 <sup>8</sup> I (A)	0 0	$\frac{1300^a}{6.5}$	1500 6.5	1800 6.5	$\begin{array}{c} 2100\\ 6.5\end{array}$	2400 <sup>b</sup> 6.6	2600 7.05	0° 0
ethane 2,3-dimethylbutane 1,5-hexadiene isobutane 1-butene 4-methyl-1-pentene 3-methyl-1-butene 1,4-pentadiene 1-pentene cyclopropane methane propane 2-butenes	$\begin{array}{c} 0.067\\ 0.045\\ 0.005\\ 0.15\\ 0.074\\ 0.032\\ 0.014\\ 0.003\\ 0.009\\ 0.094\\ 0.26\\ 0.018\\ \end{array}$	$\begin{array}{c} 0.087\\ 0.042\\ 0.005\\ 0.16\\ 0.067\\ 0.062\\ 0.015\\ 0.009\\ 0.010\\ 0.097\\ 0.30\\ 0.027\\ \end{array}$	0.097 0.050 nd 0.17 0.12 0.069 0.016 0.011 0.012 0.012 0.012 0.11 0.30 0.027	$\begin{array}{c} 0.10\\ 0.082\\ 0.022\\ 0.23\\ 0.13\\ 0.017\\ 0.015\\ 0.021\\ 0.032\\ 0.14\\ 0.39\\ 0.047\\ \end{array}$	$\begin{array}{c} 0.12\\ 0.22\\ 0.092\\ 0.46\\ 0.45\\ 0.42\\ 0.032\\ 0.037\\ 0.047\\ 0.069\\ 0.23\\ 0.77\\ 0.042\\ \end{array}$	$\begin{array}{c} 0.12\\ 0.32\\ 0.15\\ 0.76\\ 0.92\\ 0.69\\ 0.052\\ 0.062\\ 0.062\\ 0.10\\ 0.54\\ 0.92\\ 0.072\\ \end{array}$	$\begin{array}{c} 0.16\\ 0.43\\ 0.24\\ 0.92\\ 1.24\\ 1.12\\ 0.089\\ 0.12\\ 0.094\\ 0.21\\ 0.57\\ 0.99\\ 0.12\\ \end{array}$	$\begin{array}{c} 0.042\\ 0.034\\ 0.014\\ 0.055\\ 0.087\\ 0.082\\ 0.017\\ 0.014\\ 0.014\\ 0.014\\ 0.077\\ 0.14\\ 0.026\\ \end{array}$

<sup>a</sup> The center of plateau. <sup>b</sup> The end of plateau. <sup>c</sup> Data refer to room temperature.



**Figure 1.** Dependence of the yields for molecular products of propylene dissociation on the applied potential: ( $\Delta$ ) allene, ( $\blacktriangle$ ) propyne, (X) ethylene, (O) acetylene. Dashed line represents the current-voltage characteristics of the ionization chamber.

result measured at room temperature in the absence of the electric field was included. The effect of temperature on the yields of acetylene, ethylene, allene, and propyne is slight in the absence of applied potential; M/N for these products at 195 K is diminished by  $\sim 5-8\%$  as compared with the results obtained at ambient temperature. However, the yields of some free-radical products were greatly enhanced at lower temperature.

Some minor products, not included in Table I, were observed: *n*-butane (0.009, 0.045), isopentane (0.01, 0.01), 1-hexene (0.012, 0.042), and 2-methylpentane (0.008, 0.022). The M/N values in parentheses refer to U = 0 and 2400 V (the end of the plateau of the saturation current), respectively.

#### Discussion

Application of electric fields during radiolysis aids in estimating the contribution of excited states to the overall decomposition. This old technique, pioneered by Essex,<sup>6a</sup> was described in detail by Meisels<sup>6b</sup> and Sieck.<sup>6c</sup> The field is applied until a saturation current is reached but below a threshold for electron multiplication. The energy of accelerated electrons will not usually exceed the ionization potential of the media; thus, the electrons will mainly excite rather than ionize the encountered molecules. The production of optically forbidden states is advantageous; a serious drawback of the method is poor selectivity in exciting individual states; this is due to the broad energy spectrum of electrons (difficult to be determined both experimentally and theoretically) and to the mechanism of electron interactions with molecules involving partial energy losses.

The fast ion-molecule reactions remain unaffected despite the application of the field in the plateau range. Therefore, the products observed originate from the reactions of excited states with energies below IP (in the case of propylene, IP =  $9.74 \text{ eV}^8$ ).

The main series of experiments was performed at a temperature of 195 K. Since activation energies for alkyl radical addition to propylene are in the range 7–8 kcal mol<sup>-1,9</sup> the rate constants for addition will be diminished by 2 or 3 orders of magnitude.

The lowering of temperature to 195 K at U = 0 results in a substantial increase in the yields for ethane and isobutane (see Table I), i.e., the hydrocarbons originating from methyl radical. This is due to the competition between recombination and addition of the radicals to propylene. At lower temperature the rate for addition is diminished, which makes it possible to determine the yields for the pertinent radical products. Such a method was used to advantage in the study of free-radical reactions in  $\gamma$ -irradiated gaseous ethylene.<sup>10</sup>

The enhancement in the yields for some products with increasing potential applied between the electrodes, especially marked at the end of the plateau, indicates that additional amounts of excited propylene molecules are formed in collisions with accelerated electrons and subsequently undergo dissociation. A mechanism for the product formation may be easily explained on the basis of the results of Borrel et al. (1849-Å photolysis)<sup>1a</sup> and those of Collin et al. (1630-Å photolysis).<sup>1b</sup> A somewhat modified reaction scheme, including only the primary processes, is the following:

$$C_3H_6^* = H + C_3H_5$$
 (I)

$$= CH_3 + C_2H_3 \tag{II}$$

$$= C_2 H_4 + C H_2 \tag{III}$$

$$= C_2 H_2 + C H_4$$
 (IV)

Further reactions of hydrogen atoms with propylene yield propyl radicals:

$$H + C_3 H_6 = sec - C_3 H_7^*$$
(1)

$$= n - C_3 H_7^*$$
 (2)

The interradical reactions involving propyl, allyl, vinyl, and methyl radicals are responsible for the formation of

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Figure 2. Dependence of the corrected yields for free radicals on the applied potential: ( $\Delta$ ) isopropyl, ( $\odot$ ) allyl, (O) methyl, ( $\Delta$ ) vinyl.

the majority of products assembled in Table I. Using literature data for  $k_{\rm d}/k_{\rm r}^{11}$  and our value  $k_{\rm d}/k_{\rm r} \approx 3.2$  for the reaction of vinyl and isopropyl radicals<sup>12</sup> (eq 3 and 4), we

$$C_2H_3 + i \cdot C_3H_7 = 3 \cdot \text{methyl-1-butene}$$
(3)

$$= C_2 H_4 + C_3 H_6 \tag{4}$$

could calculate the yields for the individual products depending on the applied potential. These values are given in the form  $\Delta(M/N) = (M/N)_U - (M/N)_{U=0}$ , to present only the effect of the electric field (see Figure 2). A marked difference between the yields for methyl and vinyl radicals should be noted. The effect cannot be due to the secondary dissociation of excited vinyl radicals formed in process II

$$C_2 H_3^* = C_2 H_2 + H$$
 (5)

since the increase in acetylene production is not great enough. Hydrogen-atom abstraction by vinyl radicals from propylene (eq 6) suggested by Figuera et al.<sup>3b</sup> should also

$$C_2H_3 + C_3H_6 = C_3H_5 + C_2H_4 \tag{6}$$

be rejected since additional ethylene is not formed. A separate series of experiments presents evidence that such a reaction does not occur.<sup>12</sup> Apparently the appreciable reactivity of vinyl radicals toward propylene (eq 7) is re-

$$C_2H_3 + C_3H_6 = C_5H_9 \tag{7}$$

sponsible for the discrepancies. Since the activation energy for reaction 7 is likely to be as low as 4 kcal  $mol^{-1}$  or even less, the lowering of temperature to 195 K will not be sufficient to inhibit the occurrence of this reaction so completely as in the case of other radicals. Thus, the yield for methyl radicals may be taken as a measure for the yield of process II. The slight contribution of the dissociation of n-propyl radical originating from reaction 2

$$n - C_3 H_7^* = C H_3 + C_2 H_4 \tag{8}$$

is unimportant, as is evidenced by the small yield of ethylene, let alone the fact that this ethylene may be formed in some other processes.

The yield for process I can be estimated by summing the yields for allyl radicals, allene, and propyne. Allene originates from the dissociation of allyl radicals, as is established by Collin in 1630-Å photolysis of propylene: <sup>16</sup>

$$C_{3}H_{5}^{*} = C_{3}H_{4} + H$$
 (9)

However, the formation of propyne deserves some additional remarks. The elimination of molecular hydrogen from propylene, analogous to the reaction observed in ethylene, is not likely to occur. Although the activation barrier for this process is small, it was observed neither in mercury photosensibilization nor in 1630- and 1849-Å photolyses.<sup>1,2</sup> Excited CH<sub>3</sub>C=CH<sub>2</sub> and CH<sub>3</sub>CH=CH radicals, products of a primary breakage of the vinyl C-H bond, could have been propyne precursors (see eq 10 and 11). Other channels for the dissociation of these radicals

$$CH_3\dot{C} = CH_2 * = CH_3C = CH + H$$
(10)

$$CH_{3}CH = \dot{C}H^{*} = CH_{3}C \equiv CH + H$$
(11)

are also available (see eq 12 and 13). The fact that the

$$CH_3C = CH_2 * = CH_2 = CH_2 + H$$
 (12)

$$CH_3CH = CH^* = CH_3 + C_2H_2$$
 (13)

potential dependence of the yields for allene and propyne is exactly similar (indicating a common precursor for both hydrocarbons) may be taken as an argument against this hypothesis, although we admit that the argument is not conclusive. From radiolysis and vacuum UV photolysis of 1-butene, it also follows that allene and propyne have a common precursor. The ratio propyne/allene increases with increasing excitation energy and is independent of pressure.<sup>7</sup> In this case the formation of  $C_3H_5$  radicals having a vinylic structure by the simple cleavage of either C-C or C-H bonds is not possible. Thus, the question is not settled; further investigations are needed. It may only be taken for granted that propyne originating from decomposing propylene must be formed through a rupture of the C-H bond; consequently, its yield is included in process I.

The contribution of process III is slight under our experimental conditions; it is evidenced by the small yields for 2-butenes (see Table I), and the yield for ethylene after the contribution of reaction 4 has been allowed for. The yield for 2-butenes increases by  $\Delta(M/N) \approx 0.1$  with the increase in potential from 1300 to 2600 V. It agrees well with the results of photolytic experiments.<sup>1</sup> At 1849 and 1630 Å the quantum yields for process III are 0.03 and 0.02, respectively.

It is difficult to assess the contribution of process IV. The enhancement in acetylene yield over the range of potentials 1300–2400 V is  $\sim 0.35$ . There are additional routes for acetylene formation: disproportionation of vinyl radicals<sup>13</sup> and dissociation of excited vinyl radicals in reaction 5. Ultimately the contribution of process IV is small as compared with processes I and II.

To complete the picture of dissociation channels, the formation of small amounts  $(M/N \approx 0.1 \text{ at } 2400 \text{ V})$  of cyclopropane should be mentioned. Process V can be suggested:<sup>2</sup>

$$C_3H_6^* = c - C_3H_6$$
 (V)

Finally, it may be concluded that processes I and II are the main contributors to the dissociation of propylene excited by the impact of slow electrons.

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TABLE II:Dependence of the Yields for the MainDissociation Channels of Excited Propylene Moleculeson the Applied Potential

poten pro- cess	tial (eV)		1500	1800	2100	2400
I	$\begin{array}{c} C_{3}H_{6}^{*} \rightarrow \\ H + C_{2}H_{6} \end{array}$	$\Delta(M/N)$	0.22 72	0.42 68	1.3 62	2.7 60
п	$C_{3}H_{6}^{*} \rightarrow CH_{3}^{+} + C_{2}H_{3}^{+}$	$\Delta(M/N)$ %	0.085 28	0.195 32	0.78 38	1.8 40
II/I	<i>, , , , , , , , , ,</i>		0.39	0.47	0.60	0.66

The dependence of the yields and relative contributions of processes I and II on the potential applied over a plateau range is shown in Table II. The contribution of process II increases with increasing potential. At higher electron energies excitation to higher electronically excited states is expected. It is of interest to examine whether this trend will be observed, considering the dependence of the ratio of processes II vs. I on the excitation energy of the vibrationally excited propylene in the ground electronic state. RRKM calculations (the details are given in the Appendix) show that the dependence is indeed much similar (see Figure 3). The points plotted in the figure refer to literature data: mercury-sensitized photolysis,<sup>2</sup> chemical activation,<sup>3a</sup> and vacuum UV photolysis at 1849,<sup>1a</sup> 1630,<sup>1b</sup> and 1470 Å.<sup>14</sup>

However, these results are in sharp conflict with those obtained in the study of propylene, dissociating as a result of the photochemical activation of diazo-n-propane, where it is claimed that process II is the predominant decom-position pathway.<sup>3b</sup> We think that the mechanism advanced by Figuera et al. may be in error on three points: (1) The occurrence of hydrogen abstraction from propylene by vinyl radicals (reaction 6) is assumed; such a reaction does not occur.<sup>12</sup> (2) The assertion that CH<sub>3</sub>CH<sub>2</sub>CH radical undergoes isomerization to propylene before dissociation may not be true. A cleavage of the C-C bond before isomerization is also likely. The threshold energy needed to break the bond would be partly compensated by the formation of a double bond in the vinyl radical. (3) The confirmation of the experimental results by RRKM calculations is dubious since a too low threshold energy for process II was arbitrarily applied.

A comparison of our experimental and calculated (RRKM) results is only qualitative. In the experiments the gross processes are observed; i.e., a total of the decomposition products originating from the different excited states of the propylene molecule is determined. It is unknown whether dissociating species are excited electronically, or perhaps only decomposition of vibrationally excited levels of the ground state, formed as a result of radiationless transition from the upper states, is involved.

Both processes are likely to occur. However, good agreement between the calculations and the experimental results (obtained by using different techniques:  $\beta$  radiolysis, direct photolysis, chemical activation) is promising.

The results of the present work do not agree in many important details with those obtained by the technique of "simulated radiolysis":<sup>4</sup> (1) The ratio for processes II vs. I estimated by Derai and Danon in dependence on the electron energy is as follows:

(eV)	4	5	6	7.	8	9	10
II/I	6	6	3.5	0.5-1	<0.54	0.4-1.1	0.15-2

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**Figure 3.** (a) Dependence of the ratio of the yields for processes II and I on the applied potential: (O) experimental points. (b) Dependence of the ratio of the rate constants for dissociation according to paths II and I on the excitation energy of the propylene molecule: (solid curve) RRKM calculations; (O) ref 2, ( $\bullet$ ) ref 3a, ( $\Box$ ) ref 1a, ( $\Delta$ ) ref 1b, ( $\Delta$ ) ref 14.

According to Derai and Danon the triplet state  $T_1$  formed in the energy range 4–6 eV decomposes mainly through process II. The results obtained in the mercury  $Hg(^{3}P_{1})$ photosensitized dissociation of propylene (E = 4.9 eV) could be ascribed to the excitation of propylene in the second triplet state  $T_2$  (E = 6.1 eV). But in the latest experiments on the electron energy-loss spectrum of propylene, the very existence of this state was denied.<sup>15</sup>

(2) In simulated radiolysis the contribution of process III approaches 30-40% at an electron energy of 7-8 eV. Under our experimental conditions the contribution of this process does not exceed 1%.

(3) The threshold energies assessed from the appearance curves are 8.0 and 10.2 eV for allene and propyne, respectively. Thus, the formation of propyne would involve a superexcited state with an energy greater than the ionization potential. Our data presented in Figure 1 do not confirm this conclusion.

The reasons for these discrepancies cannot be explained readily. They appear to be due to the difference in experimental conditions. The pressure in simulated radiolysis is necessarily so low that the radicals react mainly on the walls rather than in the gas phase. The adsorption and wall-catalyzed processes may be of importance. This probably accounts for the lack of self-consistency in the obtained results. For instance, appearance curves for 1-

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70, 3844 (1979); (b) A. Kuppermann, W. M. Flicker, and A. Mosher,
Chem. Rev., 79, 77 (1979).

TABLE III: Data for the Decomposition Complex Model  $C_2H_3 \cdots CH_3^a$ 

frequency changes:	<b>1045 → 150</b>
	<b>963 → 150</b>
	920 → 0
	$578 \rightarrow 100$
	<b>428 → 100</b>
	$225 \rightarrow \text{free rotation}$
$(r^{\dagger}/r_{o})(\mathbf{C}-\mathbf{C})$	3.0 <sup>b</sup>
$[I_{A}^{\dagger}/I_{B}^{\dagger}/I_{C}^{\dagger}/(I_{A}I_{B}I_{C})]^{1/2}$	4.9 <sup>c</sup>
In CONCREDUN	$4.7  imes 10^{-40}  ext{ g cm}^2$
**	8

<sup>a</sup> All frequencies are given in reciprocal centimeters. <sup>b</sup>  $r^{\dagger}/r_0 = (6D_0/RT)^{1/6}$  (ref 18a). <sup>c</sup> Calculated on the basis of bond lengths and bond angles<sup>22</sup> assuming  $r^{\dagger}/r_0$ (C-C) = 3.0.

butene and isobutane, corresponding to the dissociation of propylene according to processes I and II followed by the reactions of free radicals, should be very similar (although not identical), whereas according to the experiments isobutane is formed at a much greater energy. Apparently some hydrogen atoms or isopropyl radicals are lost. Danon's mechanism of propylene dissociation in the triplet state  $T_1$  (4.4 eV) through the intersystem crossing followed by decomposition from the ground state should lead mainly to the formation of allyl radicals and hydrogen atoms rather than to the scission of the C-C bond. Regardless of the details of the dissociation mechanism. the rate constants for both processes calculated by RRKM methods are on the order of  $10^7 \text{ s}^{-1}$ ; therefore, both can occur only at pressures lower than ca. 5 torr. Also, direct dissociation in the vibrationally excited triplet state should be readily quenched by collisions at pressures exceeding 10 torr. Thus, the triplet state  $T_1$  should be of no importance in the conventional radiolysis studied at much greater pressures.

In the absence of the applied field, the ratio of the yields of methyl radical to the total yield for allene, propyne, and allyl radical cannot be used to estimate the yields for processes II and I in radiolysis since the methyl radical may arise from other processes, such as fragmentation of excited ions. However, our results can be used to estimate, albeit roughly, the energy of excited neutral propylene molecules in radiolysis in the absence of the field. The ratio of the yields for allene and allyl radicals provides a basis for such an assessment since the rate constant for reaction 9 should depend on the internal energy of dissociating radicals. In the presence of the external field (after subtracting a value obtained at U = 0, this ratio is 0.2 over the range 1900–2400 V and is found to enhance up to  $\sim 0.3$  at the end of a plateau (2400 V). The value agrees quite well with that of 0.2 assessed for the pressures used in the present work based on Collin's results for 1630-Å photolysis. In  $\beta$  radiolysis at U = 0, however, the ratio is as high as 1.25, which indicates that the excitation energy is appreciably higher (probably near or above the ionization potential). The observation agrees with that concerning 1-butene radiolysis—in both cases the contribution of superexcited states seems to be substantial. Vacuum UV experiments with photons having energies above 8.4 eV are needed to settle the problem.

These results can be connected with literature data on the threshold electron spectra.<sup>16</sup> Under conventional radiolytic experimental conditions in the absence of an electric field, the energies of electrons are diminished by collisions. It may be expected that, in the range of especially high cross sections, i.e., close to the ionization potential or above, the energy losses will be particularly great. One is tempted to postulate that a population of electrons in the range 6-10 eV is small. Hence, the yields for excited states in this range of energies are expected to be small as well.

# Conclusions

(1) Excited propylene molecules formed in collisions with electrons having energies below the ionization threshold decompose mainly according to processes I and II. The contribution of process II increases with increasing electron energy.

(2) The dependence of the ratio of processes II vs. I on the applied potential in radiolysis in the presence of electric fields conforms qualitatively to that calculated by RRKM methods for the vibrationally excited propylene molecule in the ground state.

(3) The excited propylene molecules formed in radiolysis have energies slightly below or higher than the ionization threshold.

(4) The results obtained by the method of "simulated radiolysis" for various reasons (too low pressure, wall effects) fail to give an accurate estimate of the events occurring in conventional radiolytic studies.

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# Appendix

RRKM Calculations. Process I. The threshold energy for the dissociation of propylene yielding atomic hydrogen and allyl radical,  $\epsilon_0 = 84.7$  kcal mol<sup>-1</sup>, was calculated by using  $\tilde{D}^{0}(n-C_{3}H_{7}-H) = 96.2$  kcal mol<sup>-1</sup> (ref 17) and allyl resonance energy (ARE) =  $11.5 \text{ kcal mol}^{-1}$  (ref 18) and assuming that activation energy for the reverse reaction is zero at 0 K. The structure for the activated complex was that proposed by Rabinovitch et al.,<sup>3a</sup> except for the assumption of two 70-cm<sup>-1</sup> frequencies for the bending motions of hydrogen atom. These values are lower than those proposed by Rabinovitch  $(2 \times 150 \text{ cm}^{-1}, \text{ complex})$  $II_{150}$ ). According to Golden et al. the reactivity of allyl radicals in recombination reactions is analogous to that of alkyl radicals.<sup>19a</sup> Therefore, the activated complex for the dissociation of propylene into allyl and hydrogen atom should have a looser structure than the association complex H + olefin for which  $2 \times 150$  cm<sup>-1</sup> frequencies of the bending motions were proposed.<sup>19</sup> The replacement of 70-cm<sup>-1</sup> frequency by some other value does not alter the course of the curve shown in Figure 3b; however, it will be shifted either upward or downward. Our model for the activated complex gives the best agreement with the ratio of processes II vs. I obtained in our experiments and with the results of vacuum UV photolyses. For this complex  $\log A_1 = 15.45.$ 

Process II. The threshold energy  $\epsilon_0 = 90.5 \text{ kcal mol}^{-1}$ is calculated on the basis of the heats of formation at 0 K kcal mol}{-1}:  $\Delta H_f^{\circ}(CH_3) = 35.8^{20} \Delta H_f^{\circ}(C_2H_3) = 63.2^{20}$  and  $\Delta H_f^{\circ}(C_3H_6) = 8.47^{21}$  (the activation energy for the reverse

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reaction is assumed to be zero at 0 K). The value is appreciably higher than that used by Figuera et al. ( $\epsilon_0$  = 81-83.75 kcal mol<sup>-1</sup>).<sup>3b</sup> Parameters for the activated complex are summarized in Table III; the frequencies of the propylene molecule are taken from the work of Rabinovitch.<sup>3a</sup> Based on this complex the preexponential factor for the reverse reaction is  $\vec{A} = 10^{10} \text{ L} \text{ mol}^{-1} \text{ s}^{-1}$ , i.e., a value similar to the one in the case of alkyl radicals.

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of molecular vibrational and vibrational-rotational quantum states.<sup>23</sup> The values for individual microscopic rate constants are burdened with an error due to the treatment of hindered rotations in the propylene molecule as oscillations that have a constant frequency of 225 cm<sup>-1</sup>, independently of the energy.<sup>24</sup> The error is automatically compensated for in calculations of the ratio  $k_{\rm II}/k_{\rm I}$ , since the latter one does not depend on the density of the quantum states in the active molecule.

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# Kinetics Study of the Reactions of NO with FO, CIO, BrO, and IO at 298 K

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The reactions of nitric oxide with halogen oxide radicals (XO = FO, ClO, BrO, IO) have been studied at 298 K by utilizing the discharge flow/mass spectrometric technique. The pseudo-first-order decays of XO radicals were measured in the presence of large excess concentrations of nitric oxide. The bimolecular rate coefficients and their associated  $2\sigma$  uncertainties are as follows (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>):  $k(NO + FO) = (2.60 \pm 0.50) \times 10^{-11}$ ,  $k(\text{NO} + \text{ClO}) = (1.72 \pm 0.18) \times 10^{-11}, k(\text{NO} + \text{BrO}) = (2.15 \pm 0.18) \times 10^{-11}, k(\text{NO} + \text{IO}) = (1.67 \pm 0.16) \times 10^{-11}.$ In addition, the rate coefficient for the reaction of atomic oxygen with molecular iodine was determined at 298 K by observing the pseudo-first-order decay of  $I_2$  in the presence of a large excess concentration of atomic oxygen. The result is  $k(O + I_2) = (1.38 \pm 0.44) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These results are compared to previous measurements.

#### Introduction

In recent years, there has been considerable interest in the chemical reactions of atmospheric halogen-containing trace molecules. Most of this interest has centered around chlorine-containing species<sup>1</sup> and, more recently, those containing bromine<sup>2</sup> because of their proposed roles in the destruction of stratospheric ozone. The reactions of molecules containing fluorine or iodine have received far less attention because of the predicted low efficiency of the inorganic forms of fluorine for catalytic ozone destruction and the lack of a significant source of stratospheric iodine. Recent measurements of stratospheric HF have yielded HF altitude profiles that are in fair agreement with photochemical model predictions.<sup>3</sup> However, earlier concentration measurements were lower by as much as a factor of 4, which may suggest a more important role for fluorine compounds in the catalytic destruction of ozone than is generally expected.<sup>4-6</sup> In addition, it has recently been suggested that iodine compounds may play a significant role in the control of ozone levels in the planetary boundary layer, particularly in remote marine areas.<sup>7</sup>

In all four systems of halogen-containing compounds, reactions<sup>8</sup> Ia-d play an important role in controlling the

$$NO + FO \rightarrow NO_2 + F$$
  $\Delta H^{\circ}_{298} = -20.7 \text{ kcal mol}^{-1}$  (Ia)

 $NO + ClO \rightarrow NO_2 + Cl$  $\Delta H^{\circ}_{298} = -9.0 \text{ kcal mol}^{-1}$ (Ib)  $NO + BrO \rightarrow NO_2 + Br$   $\Delta H^{\circ}_{298} = -16.8 \text{ kcal mol}^{-1}$ (Ic)

 $NO + IO \rightarrow NO_2 + I$   $\Delta H^{\circ}_{298} = -27 \text{ kcal mol}^{-1}$  (Id)

ratio [X]/[XO], and reaction Ib (NO + ClO) directly controls the magnitude of [ClO] in the stratosphere.<sup>9</sup> In spite of the general importance of reactions Ia-d, there are no studies of the kinetics of reactions Ia (NO + FO) and Id (NO + IO) currently in the literature. In addition, there was only one relatively reliable value of the bimolecular

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