n

The combination of HOCl formation and removal leads to a net destruction of ozone via the cycle

$$HO_2 + ClO \rightarrow HOCl + O_2$$
 (3)

$$HOCl + h\nu \rightarrow OH + Cl$$
(4)

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{19}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{20}$$

et:
$$2O_3 \rightarrow 3O_2$$
 (21)

In addition, HOCl formation plus photolysis converts HO_2 to OH (combination of reactions 3 and 4). This results in an enhanced CIO_x effect on O_3 due to the reaction

$$OH + HCl \rightarrow H_2O + Cl$$
 (22)

which releases radical chlorine from the reservoir species.

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Ion-Molecule Reactions and Thermal Decomposition of Ions in N_2-O_2 -Alkane (C_2-C_8) Mixtures Studied by Time-Resolved Atmospheric Pressure Ionization Mass Spectrometry

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The experiments were carried out at temperatures ranging from 236 to 569 K. The O_2^+ ion reacted with *n*-alkanes (C_nH_{2n+2}) via fast nondissociative and dissociative charge-transfer channels, its proportion depending on temperature. The nondissociative product $C_nH_{2n+2}^+$ subsequently reacted with O_2 via a slow H atom transfer path, producing alkyl ions. With increasing temperature the alkane ions $C_nH_{2n+2}^+$ ($n \ge 4$) began to decompose thermally, producing olefinic ions and alkanes. The product olefinic ions $C_mH_{2m+2}^+$ ($m \ge 4$, 5, 6) reacted with O_2 via a slow H atom transfer path, producing alkenyl ions $C_mH_{2m-1}^+$. The $C_8H_{1n}^+$ decomposed thermally forming fragment alkyl ions and olefins. The fragment alkyl ions reacted with n- C_8H_{18} reproducing $C_8H_{17}^+$, thus leading to a chain mechanism in n- C_8H_{18} decomposition. The equilibrium reaction, $C_2H_5^+ + C_2H_6 \rightleftharpoons C_4H_{11}^+$, and the subsequent dissociative rearrangement reaction, $C_4H_{11}^+ \rightarrow C_4H_9^+ + H_2$, were studied. The reactions of NO⁺ and NOO⁺, both minor products of the irradiation of N_2 - O_2 mixtures, with alkanes were also studied. The rate constants of the ion-molecule reactions and the unimolecular thermal decomposition reactions and the equilibrium constant were measured.

Introduction

Ion-molecule reactions and thermal decomposition of ions occurring in N_2 -O₂-alkane mixtures under high-pressure conditions are important processes in some fundamental fields. Elucidation of the O₂-adding effect on ion reactions in hydrocarbons is of special interest to radiation chemistry, since both O₂ and hydrocarbons are important and much studied molecules and, in addition, O₂ is sometimes used as a radical scavenger in the radiolysis. Thermal decomposition of alkyl ions is interesting because it causes ionic chain reactions in the radiation-initiated thermal cracking of hydrocarbons.¹

Our time-resolved atmospheric pressure ionization mass spectrometer is suitable to study such ion processes in gases.

Experimental Section

A time-resolved atmospheric pressure ionization mass spectrometer (TRAPI) was used. Its details were described previously.^{2,3} Therefore only a brief summary will be given here. A time-resolving function is added to a usual atmospheric pressure ionization mass spectrometer (API)⁴ using repetitive X-ray pulses (2 ns duration and 6.25–100 pulses/s) for ion generation. Dose per X-ray pulse is 35 mR which produces 7.3×10^7 ions cm⁻³ in nitrogen gas at standard temperature and pressure conditions. Part of ions thus produced flow out through a pinhole aperture (11 μ m diameter and 25 μ m long) into the vacuum chamber and, after being mass analyzed by a quadrupole mass spectrometer, are detected by using an ion multiplier together with a conventional 100-MHz pulse-counting equipment, then forming a mass spectrum and a time-dependence curve of mass analyzed ion intensity. At the latter stage of the experiments a high-speed multichannel scaler used so far to obtain time-dependence curves was replaced with a new one (Seiko EG&G, DS-202D; minimum channel width 1 μ s), which was combined with a personal computer (NEC, PC-9801), a minidisk unit, a printer, and a X-Y plotter.

Standard gases in cylinders (Seitetsu Kagaku Co.) of individual N₂-alkane (C_2H_6 , C_3H_8 , n- C_6H_{14} , n- C_8H_{18} ; 20 ppm) mixtures

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Thermal Decomposition of Ions in N2-O2-Alkane Mixtures



Figure 1. Typical mass spectra obtained for (1) $N_2-O_2(1050 \text{ ppm})-C_2H_6(1.42 \text{ ppm})$ at 302 K; (2) $N_2-O_2(1050 \text{ ppm})-C_3H_8(1.18 \text{ ppm})$ at 302 K; (3 and 3') $N_2-O_2(200 \text{ ppm})-n-C_4H_{10}(1.00 \text{ ppm})$ at 301 and 491 K; (4 and 4') $N_2-O_2(1900 \text{ ppm})-n-C_6H_{14}(1.03 \text{ ppm})$ at 300 and 499 K; (5 and 5') $N_2-O_2(4100 \text{ ppm})-n-C_8H_{18}(1.95 \text{ ppm})$ at 300 and 498 K. The ions produced from N_2-O_2 components, i.e., N_2^+ (a), NO⁺ (b), O_2^+ (c), NOO⁺ (d), O_4^+ (e), and their N_2 cluster ions, are labeled only in the mass spectrum 1 for simplicity.

were used. These gases were diluted with the N_2 - O_2 (35-10000 ppm) gases in order to give appropriate alkane and O_2 contents in the reactant gases. The alkane contents were measured by gas chromatography and the oxygen contents by a concentration cell type oxygen analyzer. The experiments were carried out at temperatures ranging from 236 to 569 K and at atmospheric pressure.

Results and Discussion

1. Mass Spectra and Formation of O_2^+ , NO^+ , and NOO^+ . Mass spectra give information about ions participating in reactions. Figure 1 shows typical spectra for the N_2 - $O_2(200-4100 \text{ ppm})$ alkane(~1 ppm) mixtures at 300 and 500 K. They were obtained while pulsing and correspond to average intensities during a time interval of 180 μ s beginning at 35 μ s after the pulse irradiations. (Drift time of ions passing through the quadrupole rods of the mass spectrometer is somewhat longer than 35 μ s.)

In atmospheric pressure $N_2-O_2(\sim 1000 \text{ ppm})$ mixtures, N_4^+ and N_3^+ are formed instantaneously by the irradiations. Subsequently, they change to O_2^+ , NO^+ , and NOO^+ within a few microseconds by reactions with O_2 . The NOO⁺ ions, which have a different structure from the well-known ONO^+ ,^{3,5} decompose thermally to $NO^+ + O$ with a rate constant of 5.6 × 10⁷ exp(-4500/RT) s^{-1,3} The formation ratio of O_2^+ to $NO^+ + NOO^+$ is 4.7⁶ and that of NOO⁺ to NO⁺ is 1.7 at 303 K.³ The O_2^+ , NO^+ , and NOO⁺ react with alkanes (C_nH_{2n+2}) forming alkane ions, alkyl



Figure 2. Time-dependence curves of the major ion intensities observed in N_2 -O₂(1050 ppm)-C₂H₆(1.42 ppm) at 302 K. The O₂⁺ curve is shifted to the right to avoid overlapping with the NO⁺ curve.

ions, olefinic ions, and alkenyl ions. The N_2^+ ions observed in Figure 1 are formed by the irradiation of rarefied buffer N_2 gas outside the reactor and so disappear rapidly by diffusion.² The impurity ions observed, mainly H_2O cluster ions, are insignificant in amounts owing to the initial short observation time: such time interval was used to study reactions without interference of impurities.

2. $O_2^+ + C_n H_{2n+2}$ and $C_n H_{2n+2}^+ + O_2$ Reactions. 2.1. Ethane. Figure 2 shows time-dependence curves of the major reactant and product ions in N₂-O₂(1050 ppm)-C₂H₆(1.42 ppm) mixtures at 302 K. The rate constant of $O_2^+ + C_2H_6$ reaction can directly be obtained from the decay slope of O_2^+ and the concentration of C_2H_6 . The decay of ions due to diffusion to the reactor wall and charge neutralization in gas volume is only about 15% per 300 μ s over the temperature region studied here.^{2,6} Therefore, it did not interfere with the determination of reaction rate constants. The detailed procedures are given in ref 2. Reaction rate constants measured here are summarized in Table I. N2 cluster ions $O_2^+ \cdot nN_2$ gave the same decay slope as the bare ion O_2^+ did. This was the general observation for the N_2 cluster ions of other bare ions. Effect of N_2 clustering on the reaction rate constant will be discussed later. The reaction model is inferred from Figures 1 and 2 as follows:

$$O_2^+ + C_2 H_6 \rightarrow C_2 H_6^+ + O_2 + 0.6 \text{ eV}$$
 (1a)

$$\rightarrow C_2 H_5^+ + HO_2 + 1.5 \text{ eV}$$
 (1b)

(Thermochemical data used here were obtained from ref 7 and 8.) Although the m/z 30 curve consists of $C_2H_6^+$, isotope peak

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| TABLE I: | Reaction Rate | Constants Measu | ared in the Present | Experiments |
|----------|----------------------|------------------------|---------------------|-------------|
| | | | | |

| reaction | rate const, cm ³ s ⁻¹ | temp, K (comments) | | |
|--|---|--|--|--|
| · · · · · · · · · · · · · · · · · · · | Ion-Molecule Reaction | | | |
| $O_2^+ + C_2H_2 \rightarrow C_2H_2^+ + O_2$ | $(1.21 \pm 0.20) \times 10^{-9}$ | 236-458 | | |
| $O_2^+ + C_2H_0 \rightarrow C_2H_0^+ + O_2$ | $(1.36 \pm 0.21) \times 10^{-9}$ | 302 | | |
| $O_2^+ + r_0 C_1 H_1 \rightarrow C_1 H_1^+ + O_2 (\sim 84\%)$ | $(1.50 \pm 0.21) \times 10^{-9}$ | 301 (product distributions | | |
| $O_2 + n^2 C_4 \Pi_{10} + C_4 \Pi_{10} + O_2 (-0.476)$ | $(1.40 \pm 0.23) \times 10$ | depend on temperature (see text)) | | |
| $- C U^{\dagger} + U + O (-1\%)$ | | depend on temperature (see text)) | | |
| $\rightarrow C_4 n_8 + n_2 + O_2 (\sim 1\%)$ | | | | |
| $\rightarrow C_3 H_7 + CH_3 + O_2 (\sim 15\%)$ | (1.00. (0.00)) (| 200 (1 1 1 1 | | |
| $O_2^+ + n O_6 H_{14} \rightarrow C_6 H_{14}^+ + O_2^- (~/3\%)$ | $(1.99 \pm 0.30) \times 10^{-5}$ | 300 (product distributions | | |
| | | depend on temperature (see text)) | | |
| $\rightarrow C_3 H_7^+ + C_3 H_7 + O_2 (\sim 2\%)$ | | | | |
| $\rightarrow C_4 H_7^+ + H + C_2 H_6 + O_2 (\sim 2\%)$ | | | | |
| $\rightarrow C_4 H_8^+ + C_2 H_6 + O_2 (\sim 6\%)$ | | | | |
| $\rightarrow C_4 H_9^+ + C_2 H_5 + O_2 (\sim 10\%)$ | | | | |
| $\rightarrow C_{5}H_{11}^{+} + CH_{3} + O_{2} (\sim 3\%)$ | | | | |
| $\rightarrow C_6 H_{12} + H_2 + O_2 (\sim 3\%)$ | | | | |
| $O_2^+ + n C_8 H_{18} \rightarrow C_8 H_{18}^+ + O_2 (\sim 92\%)$ | $(1.94 \pm 0.30) \times 10^{-9}$ | 300 (product distributions | | |
| | , , | depend on temperature (see text)) | | |
| $\rightarrow C_{5}H_{11}^{+} + C_{2}H_{7} + O_{7} (\sim 2\%)$ | | | | |
| $\rightarrow C_{4}H_{12}^{+} + C_{2}H_{4} + O_{2}(\sim 4\%)$ | | | | |
| $\rightarrow C_2 H_{12}^+ + C H_2 + O_2 (\sim 1\%)$ | | | | |
| $NOO^+ + C_1H_2 \rightarrow C_1H_2^+ + NO + OH$ | $(0.89 \pm 0.15) \times 10^{-9}$ | 302 | | |
| $NOO^+ + C_2H_0 \rightarrow C_2H_0^+ + NO + OH$ | $(1.08 \pm 0.18) \times 10^{-9}$ | 302 | | |
| $NOO^{+} + * C H \rightarrow C H^{+} + NO + OH$ | $(1.08 \pm 0.18) \times 10^{-9}$ | 301 | | |
| NOO ⁺ + $n \cdot C_4 n_1 = C_4 n_9$ + NO + OH | $(1.03 \pm 0.21) \times 10^{-9}$ | 200 | | |
| NOO ⁺ + $n \cdot C_6 \Pi_{14} \rightarrow C_6 \Pi_{13}^+$ + NO + OH | $(1.33 \pm 0.30) \times 10^{-9}$ | 300 | | |
| $NOO^{+} + h C_8 H_{18} \rightarrow C_8 H_{17}^{+} + NO + OH$ | $(1.70 \pm 0.40) \times 10^{-10}$ | 300 500 (1 1 1 1 m) (1 1 m) | | |
| $NO^{+} + n - C_6 H_{14} \rightarrow C_6 H_{13}^{+} + HNO$ | $(1.85 \pm 0.40) \times 10^{10}$ | 300-508 (insignificant | | |
| | (1.0.) (0.) (0.) (0.) | temperature dependence) | | |
| $NO^{+} + n - C_8 H_{18} \rightarrow C_8 H_{17}^{+} + HNO$ | $(4.9 \pm 1.0) \times 10^{-10}$ | 300–483 (insignificant | | |
| | | temperature dependence) | | |
| $C_2H_6^+ + O_2 \rightarrow C_2H_5^+ + HO_2$ | $(1.15 \pm 0.35) \times 10^{-10}$ | 302 | | |
| $C_3H_8^+ + O_2 \rightarrow C_3H_7^+ + HO_2$ | $(3.3 \pm 0.6) \times 10^{-11}$ | 302 | | |
| $n - C_4 H_{10}^+ + O_2 \rightarrow C_4 H_9^+ + HO_2$ | $(7.5 \pm 2.0) \times 10^{-13}$ | 301 | | |
| $n-C_6H_{14}^+ + O_2 \rightarrow C_6H_{13}^+ + HO_2$ | $(4.2 \pm 1.0) \times 10^{-13}$ | 300 | | |
| $n-C_8H_{18}^+ + O_2 \rightarrow C_8H_{17}^+ + HO_2$ | $(1.4 \pm 0.7) \times 10^{-14}$ | 300 | | |
| $C_{3}H_{6}^{+} + n - C_{4}H_{10} \rightarrow C_{4}H_{8}^{+} + C_{3}H_{8}$ | $(7.3 \pm 1.5) \times 10^{-10}$ | 498 ($C_3H_6^+$ formed by the | | |
| | | decomposition of $n-C_4H_{10}^+$) | | |
| $C_4H_8^+ + O_7 \rightarrow C_4H_7^+ + HO_7$ | $(4.7 \pm 1.2) \times 10^{-14}$ | 500 ($C_4H_8^+$ formed by thermal | | |
| | | decomposition of $n-C_{2}H_{12}^{+}$ | | |
| $C_{\epsilon}H_{10}^{+} + O_{2} \rightarrow C_{\epsilon}H_{0}^{+} + HO_{2}$ | $(1.7 \pm 0.4) \times 10^{-13}$ | 444-534 (C ₆ H ₁₀ ⁺ formed by thermal | | |
| | | decomposition of $n-C_{\circ}H_{1\circ}^{+}$. | | |
| | | k temperature independent) | | |
| $C_{1}H_{1}^{+} + O_{2} \rightarrow C_{2}H_{1}^{+} + HO_{2}$ | $(1.5 \pm 0.4) \times 10^{-13}$ | 444-534 (C.H.,+ formed by thermal | | |
| | | decomposition of n -CoHo ⁺ | | |
| | | k temperature independent) | | |
| $C_{1}H_{1}^{+} + C_{2}H_{2} \rightarrow$ | $(4.6 \pm 0.9) \times 10^{-10}$ | 302 | | |
| $c_{2}r_{5} + c_{3}r_{8}$ | $(4.0 \pm 0.9) \times 10^{-10}$ | 302 | | |
| sec-C3117 1 n-C41110 | $(7.2 \pm 0.5) \times 10^{-10}$ | 408 | | |
| | $(2.5 \pm 0.5) \times 10$ | 478 | | |
| | Thermal Decomposition ^a | | | |
| $n - C_4 H_{10}^+ \rightarrow C_2 H_4^+ + C H_4$ | $(1.4 \times 10^{14}) \exp(-20000/RT)$ | 405461 | | |
| $n - C_{c} H_{1}^{+} \rightarrow C_{a} H_{e}^{+} + C_{2} H_{c}$ | $(3.0 \times 10^{14}) \exp(-19500/RT)$ | 380-457 | | |
| $n \cdot C_0 H_{10}^+ \rightarrow C_1 H_0^+ + C_1 H_{10}$ | $(7.1 \times 10^{11}) \exp(-15000/RT)$ | 398-483 | | |
| $\rightarrow C_{\epsilon}H_{10}^{+} + C_{\epsilon}H_{0}$ | (| | | |
| $\sim_{3^{1}}$ $\rightarrow_{3^{1}}$ $\sim_{3^{1}}$ | | | | |
| $C_1H^+ \rightarrow C_1H^+ + C_1H^-$ | $(1.3 \times 10^{13}) \exp(-21000/RT)$ | 447-543 (C.H., + from r-C.H.) | | |
| $\rightarrow C_{H_1}^{++} + C_{H_2}^{++}$ | $(1.5 \times 10^{-}, 0.0)(21000/101)$ | oro (cgillo itom #-cgills) | | |
| $\rightarrow C H + C H$ | | | | |
| $-\zeta_{6113} + \zeta_{2114}$ | | | | |
| | Rearrangement ^a | | | |
| $(C_2H_4 \cdot H \cdot C_2H_5)^+ \rightarrow sec - C_4H_6^+ + H_2$ | $(3.6 \times 10^{12}) \exp(-12000/RT)$ | $305-356 ((C_2H_3\cdot H\cdot C_2H_3)^+$ formed by | | |
| | | $C_2H_5^+ + C_2H_6$ reaction) | | |

^aRate constants in s⁻¹.

(IP) of $C_2H_5^+$ (natural abundance of ¹³C is 1.12%), and NO⁺, its shape and size suggest insignificant presence of $C_2H_6^+$. However, when we reduced the oxygen content from 1050 to 35 ppm the shape changed drastically as is shown in Figure 3. The initial convex should be attributed to $C_2H_6^+$, although the curve in the latter time stage is explained solely by the $C_2H_5^+$ IP and NO⁺. Subtracting these components from the m/z 30 curve, we obtain the $C_2H_6^+$ curve illustrated by the solid line. These observations show the occurrence of reaction 1a and a subsequent H atom transfer reaction $% \left({{{\bf{n}}_{\rm{s}}}} \right)$

$$C_2H_6^+ + O_2 \rightarrow C_2H_5^+ + HO_2 + 0.91 \text{ eV}$$
 (2)

Therefore, the time dependence of $C_2H_6^+$ intensity is written as

$$[C_{2}H_{6}^{+}] = \frac{k_{1a}[C_{2}H_{6}][O_{2}^{+}]_{0}}{k_{2}[O_{2}] - k_{1a}[C_{2}H_{6}]} \{\exp(-k_{1a}[C_{2}H_{6}]t) - \exp(-k_{2}[O_{2}]t)\} (3)$$

where $[O_2^+]_0$ is the initial concentration of O_2^+ . Since $[O_2] \gg [C_2H_6]$, $k_2[O_2]$ will be greater than $k_{1a}[C_2H_6]$. Indeed, the decay slope of $C_2H_6^+$ is equal to that of O_2^+ and so it does not give the

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Figure 3. Time-dependence curves of m/z 30 ions observed in N₂-O₂(35 ppm)-C₂H₆(1.84 ppm) at 301 K. The solid line, C₂H₆⁺, was obtained by subtracting the contribution of $C_2H_5^+$ IP and NO⁺ from the m/z 30 curve.

 k_2 value. In this case we can determine the k_2 value by the curve-fitting method. If we choose $k_2 = 1.15 \times 10^{-10}$ cm³ s⁻¹, the calculated curve by use of eq 3 just fits the solid curve in Figure 3. As the initial rising slope of $C_2H_5^+$ curve (not shown in Figure 3) is gentle compared with that of $C_2H_6^+$, reaction 1b does not seem to occur significantly irrespective of its higher exothermicity than reaction 1a. It has been generally observed that exothermic charge-transfer reactions to polyatomic molecules are fast.^{9,10} On the other hand, H⁻-transfer reactions are slow due to the internal barrier of reaction path.^{10,11} This seems to be true for reaction 1. Thus, alkyl ions $C_2H_5^+$ are formed not by reaction 1b but by the two-step reactions 1a and 2.

A reaction between excited O_2^+ and CH_4 is proposed to proceed by the following modes:¹²

$$O_2^+(a^4\pi_u) + CH_4 \rightarrow CH_4^+ + O_2 + 3.4 \text{ eV}$$
 (4a)

$$\rightarrow CH_3^+ + HO_2 + 3.8 \text{ eV}$$
 (4b)

The rate constant for reaction 4 is reported¹² to be 1.2×10^{-9} cm³ s⁻¹, and the branching ratio k_{4a}/k_{4b} to be 0.5. However, we consider from our results for C_2H_6 , C_3H_8 , C_4H_{10} , and so on (see later) that a dissociative charge-transfer reaction

$$O_2^+(a^4\pi_u) + CH_4 \rightarrow CH_3^+ + H + O_2 + 1.8 \text{ eV}$$

would be more plausible than (4b) for the CH_3^+ formation mode. For reactions between the ground-state O_2^+ and $C_n H_{2n+2}$ a dissociative path becomes exothermic only when $n \ge 4$.

In our atmospheric pressure experiments many cluster ions are observed. When nN_2 or $O_2 \cdot nN_2$ clusters to O_2^+ , the mass of the reactant ion and the reduced mass of the reactants will increase. Collision theory predicts that the collision constant between $O_2^+ nN_2$ and C_2H_6 will decrease from 1.25×10^{-9} cm³ s⁻¹ for bare O_2^+ (n = 0) to 0.88 × 10⁻⁹ cm³ s⁻¹ for large cluster ions (n = ∞). Since the clustering energy is weak, the abundance of the cluster ions will decrease with increasing temperature. In the $N_2-O_2(1050)$ ppm)– $C_2H_6(1.42 \text{ ppm})$ mixtures, the abundance ratio of the bare O_2^+ to $\sum_{n=0}^{\infty}(O_2^+ \cdot nN_2 + O_2^+ \cdot O_2 \cdot nN_2)$ changed from 0% at 236 K to 85% at 485 K and the ratio of $O_2^+ \cdot O_2 \cdot nN_2$ to $\sum_{n=0} (O_2^+ \cdot nN_2)$

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+ $O_2^+ O_2 nN_2$) changed from >90% at 236 K to 0% at 458 K. Irrespective of these large variations of clustering, 10 measured rate constants of reaction 1 over these temperatures were within the range of $(1.15 \pm 0.12) \times 10^{-9}$ cm³ s⁻¹, although a slight increase of the value was observed with increasing temperature. This will show that the rate constant of $O_2^+ + C_2H_6$ reaction is nearly the same as that of $O_2^+ \cdot O_2 + C_2H_6$ reaction and further that the N_2 cluster ions may be mainly formed outside the reactor by adiabatic cooling through the pinhole aperture. On the other hand, Dotan et al.¹³ reported that, although the O_2^+ ion reacted with CH_4 slowly giving $CH_3O_2^+$, this reaction did not proceed for $O_2^+ O_2$ irrespective of its weak binding energy of ~9.5 kcal/mol.¹⁴

Referring to hydrocarbon ions seen in Figure 1, the abundance of their N_2 clusters is small even at room temperature and it decreases with increasing temperature to an insignificant amount. Therefore, the presence of the cluster ions would not affect the interpretation of the results given below even if they are formed in the reactor.

2.2. Propane, n-Butane, n-Hexane, and n-Octane. Similar reactions to those described above for ethane were observed. For alkanes with $n \ge 4$, dissociative charge-transfer channels opened in addition to the nondissociative one.

For C₃H₈,

$$O_2^+ + C_3 H_8 \rightarrow C_3 H_8^+ + O_2 + 1.1 \text{ eV}$$
 (5)

$$C_{3}H_{8}^{+} + O_{2} \rightarrow (n \text{ or } sec \text{ -})C_{3}H_{7}^{+} + HO_{2}$$
 (+0.69 or 1.4 eV)
(6)

For *n*-C₄H₁₀,

$$O_2^+ + n - C_4 H_{10} \rightarrow n - C_4 H_{10}^+ + O_2 + 1.6 \text{ eV}$$
 (~84%) (7a)
→ (2- or 1-) $C_4 H_8^+ + H_2 + O_2$ (+1.7 or 1.2 eV) (~1%)
(7b)

$$\rightarrow$$
 (*n*-)C₃H₇⁺ + CH₃ + O₂ (+0.30 eV) (~15%) (7c)

$$(sec- \text{ or } n-)C_4H_9^+ + HO_2 \quad (+1.0 \text{ or } 0.30 \text{ eV}) \quad (8)$$

For $n-C_6H_{14}$,

$$O_2^+ + n - C_6 H_{14} \rightarrow n - C_6 H_{14}^+ + O_2 + 1.9 \text{ eV} \quad (\sim 73\%) \quad (9a)$$

$$(n-)C_3H_7^+ + n-C_3H_7 + O_2 (+0.43 \text{ eV}) (\sim 2\%)$$
 (9b)

$$\rightarrow C_4 H_7^+ + H + C_2 H_6 + O_2 \quad (\sim 2\%)$$
 (9c)

→
$$(n-)C_4H_9^+ + C_2H_5 + O_2$$
 (+0.52 eV) (~10%) (9e)

$$\rightarrow C_5 H_{11}^+ + C H_3 + O_2 \quad (\sim 3\%) \tag{9f}$$

$$\rightarrow C_6 H_{12}^+ + H_2 + O_2 \quad (\sim 3\%) \tag{9g}$$

$$n - C_6 H_{14}^+ + O_2 \rightarrow C_6 H_{13}^+ + HO_2$$
 (10)

For n-C₈H₁₈

$$O_2^+ + n - C_8 H_{18} \rightarrow n - C_8 H_{18}^+ + O_2 ~(\sim 92\%)$$
 (11a)

$$\rightarrow C_4 H_9^+ + C_4 H_9 + O_2$$
 (<1%) (11b)

$$\rightarrow C_5 H_{11}^{+} + C_3 H_7 + O_2 \quad (\sim 2\%) \tag{11c}$$

$$\rightarrow C_6 H_{13}^{+} + C_2 H_5 + O_2 \quad (\sim 4\%) \tag{11d}$$

$$\rightarrow C_7 H_{15}^+ + C H_3 + O_2 \quad (\sim 1\%) \tag{11f}$$

$$n - C_8 H_{18}^+ + O_2 \rightarrow C_8 H_{17}^+ + HO_2$$
 (12)

The $O_2^+ + C_n H_{2n+2}$ reaction may directly produce $C_n H_{2n+1}^+$ ions (with neutral products of $H + O_2$ or HO_2) in addition to the

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Figure 4. Time-dependence curves of $C_4H_9^+$ and $C_4H_{10}^+$ in $N_2-O_2(850 \text{ ppm})-n-C_4H_{10}(0.94 \text{ ppm})$ at 302 K used to obtain the mode of the NOO⁺ + $n-C_4H_{10}$ reaction. The solid curves were obtained without taking into consideration the formation of $C_4H_9^+$ from this reaction (see text).

products described above. However, by comparison of the initial rising slope of $C_n H_{2n+2}^+$ with that of $C_n H_{2n+1}^+$, the contribution of the direct formation channel was found to be less than a few percent. We got this result from the curves (not shown) which are like those in Figure 4 (see later) but were obtained at temperatures above 460 K for the gas system with 200 ppm O₂ and 1 ppm $C_n H_{2n+2}$ $(n \ge 4)$. For such oxygen content the rising slope of $\hat{C}_n H_{2n+1}^+$ became slower and at such high temperatures reaction 15 (see later) became insignificant because of rapid thermal decomposition of NOO⁺, these making it easy to evaluate the contribution of the direct formation channel of $C_n H_{2n+1}^+$. Product distributions described above are values at 300 K, which were determined from the initial intensities of the corresponding time-dependence curves. With increasing temperature, the percentage of the nondissociated ions decreased: for $n-C_4H_{10}$, ~84% at 300 K, \sim 74% at 399 K, \sim 52% at 426 K, and \sim 12% at 491 K; for *n*-C₆H₁₄, \sim 73% at 300 K, \sim 57% at 391 K, \sim 21% at 460 K, and $\sim 6\%$ at 499 K; for $n-C_8H_{18}$, $\sim 92\%$ at 300 K, $\sim 50\%$ at 407 K, and $\sim 25\%$ at 476 K. At the same time, the distribution of the dissociative modes were also affected; for instance, $C_4H_9^+$ formation in $n-C_8H_{18}$ increased as can be seen in Figure 1. In addition, with increasing temperature the unimolecular thermal decomposition of the product $C_n H_{2n+2}^+$ ions began to occur. This will be described later. The rate constants of reactions 1a, 2, 5-12 measured here are listed in Table I. Charge-transfer reactions are seen to proceed with collision rates, while the subsequent H atom transfer reactions proceed slowly, becoming slower and slower with increasing carbon number of alkane ions. A few rate constants for the reactions

$$C_m H_{2m+1}^+ + C_n H_{2n+2}^- \rightarrow C_2 H_{2n+1}^+ + C_m H_{2m+2}^- \qquad (m < n)$$
(13)

were also measured and the values are listed in Table I.

It should be noted that in most reactions in Table I the product ion structure is not known. Two or more isomers may be formed. Isomerization may occur during or after the ions are produced. Therefore, the structures of ions participating in subsequent reactions will be even more uncertain.

3. $NO^+ + C_n H_{2n+2}$ Reactions. The H⁻-transfer reaction

$$NO^+ + C_n H_{2n+2} \rightarrow C_n H_{2n+1}^+ + HNO$$
(14)

was examined and the rate constants measured are summarized in Table I. The reaction is exothermic for *n*-alkanes of $n \ge 6$ and correspondingly the reaction proceeded for $n-C_6H_{14}$ and $n-C_8H_{18}$. These observations are in good agreement with the results of ICR apparatus by Lias et al.,¹⁵ except that the reaction rate constant



Figure 5. Time-dependence curves of $C_4H_{10}^+$ in N_2 - $O_2(200 \text{ ppm})$ -n- $C_4H_{10}(1.00 \text{ ppm})$ at various temperatures showing the occurrence of its thermal decomposition reaction: (1) 301 K; (2) 329 K; (3) 377 K; (4) 405 K; (5) 434 K; (6) 461 K.

for $n-C_6H_{14}$ measured here is about 5 times larger than their value. Temperature dependences for these reactions were not observed between 300 and 500 K.

4. $NOO^+ + C_n H_{2n+2}$ Reactions. The decay slope of NOO⁺ was enhanced by addition of the alkanes, and the following reaction was inferred:

$$NOO^{+} + C_{n}H_{2n+2} \to C_{n}H_{2n+1}^{+} + NO + OH$$
 (15)

In Figure 4 time-dependence curves of $C_4H_{10}^+$ and $C_4H_9^+$ in $N_2-O_2(850 \text{ ppm})-n-C_4H_{10}(0.94 \text{ ppm})$ mixtures at 302 K are shown. The corresponding two solid curves were calculated based on reactions 7, 8, and 13 $(C_m H_{2m+1}^+ \equiv s - C_3 H_7^+)$ and using the rate constants in Table I. Although the solid curve for $C_4H_{10}^+$ fits the experimental points, the solid curve for $C_4H_9^+$ rises more slowly than the experimental points. However, if we add reaction 15 as a source of $C_4H_9^+$ ions, the calculated curve just fits to the experimental curve. (The initial amount of NOO⁺ was chosen to be one-tenth that of O_2^+ . The contributions of diffusion loss of ions, reactions with trace amount of impurity water, and the isotope peak of $C_4H_9^+$ were taken into consideration to obtain the calculated curves.) Further, with increasing temperature the experimental curve shifted to the curve calculated without reaction 15, this being explained by a loss of NOO⁺ due to thermal decomposition. Thus, we have chosen $C_4H_9^+$ as the product of reaction 15.

5. Thermal Decomposition of $C_nH_{2n+2}^+$ and Subsequent Reactions. 5.1. Thermal Decomposition. The time-dependence curves of $C_4H_{10}^+$ ions formed in N_2 - $O_2(200 \text{ ppm})$ -n- $C_4H_{10}(1.00 \text{ ppm})$ mixtures are shown in Figure 5 for various temperatures from 301 to 461 K. They are illustrated after subtracting the contribution of the isotope peak of $C_4H_9^+$ from the m/z 58 curves. The m/z 58 curves also contain NO⁺· N_2 as a small fraction. However, since the decay slope of NO⁺ due to diffusion and reaction with impurity water is roughly equal to that of $C_4H_9^+$, the contribution of NO⁺· N_2 can also be subtracted together with $C_4H_9^+$ IP except for its initial part. The decay slope of $C_4H_{10}^+$ thus obtained is clearly seen to be enhanced with increasing temperature. This enhancement should be attributed to the following thermal decomposition reaction:

$$n - C_4 H_{10}^+ \rightarrow C_3 H_6^+ + C H_4 + 0.04 \text{ eV}$$
 (16)

The product ion was inferred from the mass spectra, the time dependence curves of $C_4H_{10}^+$ and candidate product ions, and energetic consideration. Figure 6 shows the time dependence

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Figure 6. Time-dependence curves of $C_4H_{10}^+$, $C_3H_6^+$, and $C_4H_8^+$ at 498 K showing the modes of the thermal decomposition of $C_4H_{10}^+$ and the successive reaction of the product $C_3H_6^+$.



Figure 7. Arrhenius plots of the thermal decomposition reaction rate constants of $n-C_4H_{10}^+$, $n-C_6H_{14}^+$, $n-C_8H_{18}^+$, and $C_8H_{17}^+$.

curves of $C_4H_{10}^+$ and $C_3H_6^+$ at 498 K. The $C_3H_6^+$ intensity increased corresponding to the decrease of $C_4H_{10}^+$ (see the behavior of these ions between 70 and 130 μ s; the increase of $C_3H_6^+$, however, is not so clear because of overlap with the decay curve of N_3^+ which has the same m/z).

Figure 7 shows Arrhenius plots of the decay slope of $C_4H_{10}^+$. At low temperatures reaction 8 is predominant but at high temperatures reaction 16 proceeds predominantly. Therefore, activation energy of reaction 16 was determined from the plots in the high-temperature region as 20 ± 2 kcal mol⁻¹ and its rate constant as $k_{16} = 1.4 \times 10^{14} \exp(-20\,000/RT) \, \text{s}^{-1}$.

For $n-C_6H_{14}^+$ and $n-C_8H_{18}^+$ similar thermal decomposition reactions were observed and the following modes were inferred from the mass spectra.

$$n - C_6 H_{14}^+ \to C_4 H_8^+$$
 (17)

$$n - C_8 H_{18}^+ \rightarrow C_6 H_{12}^+, C_5 H_{10}^+, C_4 H_8^+$$
 (18)

Formation of alkyl ions such as $C_4H_9^+$ and $C_5H_{11}^+$ does not seem to occur from the energetic viewpoint. It should be noted that these olefinic ions would also be produced by the dissociative charge-transfer reactions, 9 and 11, at high temperatures. Arrhenius plots of the decay slopes of $n-C_6H_{14}^+$ and $n-C_8H_{18}^+$ are given in Figure 7. Activation energies were determined as E_{17} = 19.5 ± 2 kcal mol⁻¹ and $E_{18} = 15 \pm 2$ kcal mol⁻¹. The rate constants were obtained as $k_{17} = 3.0 \times 10^{14} \exp(-19500/RT)$ s⁻¹, and as $k_{18} = 7.1 \times 10^{11} \exp(-15000/RT)$ s⁻¹.



Figure 8. Time-dependence curves of $C_6H_{12}^+$ and $C_6H_{11}^+$ in $N_2-O_2(4100 \text{ ppm})-n-C_8H_{18}(2.0 \text{ ppm})$ at 543 K showing the occurrence of the $C_6H_{12}^+$ + $O_2 \rightarrow C_6H_{11}^+$ + HO_2 reaction.

Reactions 16–18 may be explained by a similar four-center complex fission mechanism used for the pyrolysis of neutrals.¹⁶ That is



where R_1 and R_2 are alkyl radicals. Elimination of R_1H would be energetically easier for ions than for neutrals for lack of one binding electron probably in the cyclic transition state. This explains the lower activation energies observed. Preexponential factors obtained here have an ambiguity of nearly one order of magnitude due to $\pm 10\%$ errors of the activation energies. For neutral X-substituted hydrocarbons, RX (X = halogen, OH, OCH₃), elimination reactions of HX are reported to have activation energies of around 50 kcal mol⁻¹ and preexponential factors of around $10^{13}-10^{14}$ s^{-1.16}

5.2. Subsequent Reactions of the Product Olefinic Ions. The $C_3H_6^+$ ions formed by reaction 16 decreased with time and correspondingly the $C_4H_8^+$ ions increased as is shown in Figure 6. This is explained by the following H_2^- -transfer reaction:

$$C_{3}H_{6}^{+} + n - C_{4}H_{10} \rightarrow 2 - C_{4}H_{8}^{+} + C_{3}H_{8} + 0.69 \text{ eV}$$
 (19)

The reaction rate constant measured here, 7.3×10^{-10} cm³ s⁻¹ at 490 K, is somewhat higher than the reported values, (4.9–5.1) $\times 10^{-10}$ cm³ s^{-1.17,18}

The $C_4H_8^+$, $C_5H_{10}^+$, and $C_6H_{12}^+$ from reactions 17 and 18 also decreased with time and correspondingly $C_4H_7^+$, $C_5H_9^+$, and $C_6H_{11}^+$ increased. Time-dependence curves of $C_6H_{12}^+$ and $C_6H_{11}^+$ in N₂-O₂ (4100 ppm)-*n*-C₈H₁₈(2.0 ppm) at 534 K are shown in Figure 8 as an example. The decay slopes of these olefinic ions were enhanced proportionally with increasing O₂ concentration. This means the occurrence of the reaction

$$C_m H_{2m}^+ + O_2 \rightarrow C_m H_{2m-1}^+ + HO_2 \quad (m = 4-6)$$
 (20)

Reaction rate constants were measured at temperatures between 444 and 534 K and the results are summarized in Table I. Significant temperature dependences were not observed.

As can be seen in Figure 8 the $C_6H_{12}^+$ (m/z 84) intensity did not decrease to zero but remained at about one-tenth of its initial value. This may indicate that the $C_6H_{12}^+$ ions have two types of structures, the major one being reactive and the minor one much

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Figure 9. Van't Hoff plots of $K_p = [C_4H_{11}^+]/[C_2H_5^+][C_2H_6]$ and Arrhenius plots of the rate constant of $(C_2H_5 \cdot H \cdot C_2H_5)^+ \rightarrow sec \cdot C_4H_9^+ + H_2$ reaction.

less reactive. This was the same for $C_4H_8^+$ and $C_5H_{10}^+$. The product alkenyl ions $C_5H_9^+$ and $C_6H_{11}^+$ were stable in the present gas mixtures, but the $C_4H_7^+$ ions decreased to zero with the same decay slope of reactive $C_4H_8^+$, showing the occurrence of subsequent reaction.

The H₂⁻-transfer reaction between these olefinic ions and *n*-C₆H₁₄ and *n*-C₈H₁₈, similar to reaction 19, would not occur because of the following reason. The H₂⁻ transfer is reported to proceed by two-step mechanism,¹⁷ first the H⁻-transfer reaction and then H transfer. The H⁻-transfer reaction from *n*-C₆H₁₄ and *n*-C₈H₁₈ would be endothermic even for the most reactive structure of C_mH_{2m}⁺ (m = 4-6), i.e., 1-C_mH_{2m}⁺, although the overall H₂⁻ transfer reaction is exothermic. Therefore, the H₂⁻-transfer reaction does not occur.

It is interesting to note that both radical cations, i.e., alkane ions and olefinic ions, react slowly with O_2 producing corresponding alkyl and alkenyl ions.

6. Fate of $C_nH_{2n+1}^+$ in $C_nH_{2n+2}^-$. 6.1. $C_2H_5^+$. The $C_2H_5^+$ ion in C_2H_6 reacts as follows:

$$C_2H_5^+ + C_2H_6 + N_2 \rightleftharpoons C_4H_{11}^+ + N_2$$
 (21)

$$C_4H_{11}^+ \rightarrow C_4H_9^+ + H_2$$
 (22)

The time dependences of these ions at 302 K are shown in Figure 2. Since the mass number of $C_4H_9^+$ is the same as that of $C_2H_5^+\cdot N_2$, the curve labeled as $C_4H_9^+\cdot N_2$ contains partly $C_2H_5^+\cdot 2N_2$. Therefore, the initial rising slope of $C_4H_9^+\cdot N_2$ resembles that of $C_2H_5^+$ and the subsequent decrease of the curve is also affected by the presence of $C_2H_5^+\cdot 2N_2$. As the reaction time proceeds, the decay slope of $C_2H_5^+$ becomes equal to that of $C_4H_{11}^+$, showing an attainment of the equilibrium of reaction 21. The $C_4H_{11}^+$ ion would have the three center bonded structure $(C_2H_5 \cdot H \cdot C_2H_5)^+$ and the $C_4H_9^+$ ion a sec-butyl structure as was proposed by Hiraoka and Kebarle.¹⁹ In their experiments the equilibrium was not observed because of the relatively low pressures of 5 Torr. In our experiments the equilibrium constant $K_{\rm p} = [C_4 H_{11}^+] / [C_2 H_5^+] [C_2 H_6]$ could be measured from the intensities of $C_4H_{11}^+$, nN_2 and $C_2H_5^+$, nN_2 ($n \ge 0$) ions at temper-atures between 305 and 356 K. Van't Hoff plots are given in Figure 9. From the figure the enthalpy and entropy changes were obtained as $\Delta H_{21} = 12 \pm 2 \text{ kcal mol}^{-1}$ and $\Delta S_{21} = -15.7 \text{ cal mol}^{-1}$ deg⁻¹ (for $\Delta H_{21} = 12$ kcal mol⁻¹). Since the decay slope of C₂H₅⁺ becomes equal to that of $C_4H_{11}^+$, the following equation holds

$$k_{21}[C_2H_5^+][C_2H_6] = k_{22}[C_4H_{11}^+]$$
(23)

where k_{21} is an apparent second-order rate constant of the overall



Figure 10. Time-dependence curves of $C_8H_{17}^+$ in $N_2-O_2(4100 \text{ ppm})-n-C_8H_{18}(2.0 \text{ ppm})$ at various temperatures showing the occurrence of its thermal decomposition reaction: (1) 301 K; (2) 447 K; (3) 483 K; (4) 509 K; (5) 543 K; (6) 569 K.

forward reaction of 21 and $k_{21}[C_2H_6]$ is given by the decay slope of $C_2H_5^+$. Thus, k_{22} can be obtained from eq 23. Arrhenius plots of k_{22} are given in Figure 9. From the plots activation energy is obtained as $E_{22} = 12 \pm 2$ kcal mol⁻¹ and the rate constant is expressed as $k_{22} = 3.6 \times 10^{12} \exp(-12000/RT) \text{ s}^{-1}$. Hiraoka and Kebarle reported $E_{22} = 9.6 \pm 1$ kcal mol⁻¹. They further concluded that ΔH_{21} should be larger than E_{22} based on their observation of the negative temperature dependence for the $C_4H_9^+$ formation, and estimated somewhat arbitrarily $\Delta H_{21} = 13 \pm 3$ kcal mol⁻¹. The negative temperature dependence under their conditions, however, would not given an evidence of $\Delta H_{21} > E_{22}$, because the concentration of $(C_4H_{11}^+)^*$ (see reaction 6 in ref 19) should have a negative temperature dependence and therefore the $C_4H_9^+$ formation rate might show a negative temperature dependence even in a case of $\Delta H_{21} < E_{22}$. The 15% errors of our measured values mainly come from the mass number overlaps of

 C_2H_5 $\cdot nN_2$ and C_4H_9 $\cdot (n-1)N_2$ ions. 6.2. C_3H_7 \cdot , C_4H_9 \cdot , C_6H_{13} $\cdot , and C_8H_{17}$ \cdot . These ions did not react with the respective parent alkanes, unlike C_2H_5 \cdot in C_2H_6 . Formation of cluster ions C_nH_{2n+1} $\cdot C_nH_{2n+2}$ was not observed in the mass spectra at 300 K. However, since the alkane content was as low as about 1 ppm and trace impurities such as water obstructed the interpretation, a possibility can not be excluded of the occurrence of slow reactions with a rate constant less than 10^{-11} cm³ s⁻¹ for C_3H_8 and n- C_4H_{10} , and 10^{-12} cm³ s⁻¹ for n- C_6H_{14} and n- C_8H_{18} . These alkyl ions except for C_8H_{17} $^+$ were also thermally stable at least up to 500 K.

7. Thermal Decomposition of $C_8H_{17}^+$ and Subsequent Ionic Chain Reactions. The time-dependence curves of $C_8H_{17}^+$ in $N_2-O_2(4100 \text{ ppm})-n-C_8H_{18}(2.0 \text{ ppm})$ are shown in Figure 10 for various temperatures from 301 to 569 K. The decay of $C_8H_{17}^+$ ions is enhanced thermally. Mass spectra and time-dependence curves suggest the following thermal decomposition reactions:

$$C_8 H_{17}^+ \rightarrow C_6 H_{13}^+ + C_2 H_4$$
 (24a)

$$\rightarrow C_5 H_{11}^+ + C_3 H_6 \tag{24b}$$

$$\rightarrow C_4 H_9^+ + C_4 H_8 \tag{24c}$$

The $C_8H_{17}^+$ ions are produced by the reactions

$$C_8H_{18}^+ + O_2 \rightarrow C_8H_{17}^+ + HO_2$$
 (12)

$$C_m H_{2m+1}^+ + n - C_8 H_{18}^- \rightarrow C_8 H_{17}^+ + C_m H_{2m+2}$$
 (m ≤ 6)
(13')

$$NO^{+} + n - C_8 H_{18} \rightarrow C_8 H_{17}^{+} + HNO$$
 (14')

$$NOO^+ + n - C_8 H_{18} \rightarrow C_8 H_{17}^+ + NO + OH$$
 (15')

At high temperatures, say above 447 K in Figure 10, $C_8H_{18}^+$ ions

⁽¹⁹⁾ Hiraoka, K.; Kebarle, P. Can. J. Chem. 1980, 58, 2262.



Figure 11. Time-dependence curves of $C_4H_9^+$, $C_5H_{11}^+$, $C_6H_{13}^+$, and $C_8H_{17}^+$ in N_2 -O₂(4100 ppm)-*n*- $C_8H_{18}(2.0 \text{ ppm})$ at 483 K, suggesting the occurrence of ionic chain decomposition reactions.

will be decomposed rapidly with $k_{18} = 7.1 \times 10^{11} \exp(-15000/RT)$ s⁻¹. The thermal decomposition of NOO⁺ to NO⁺ proceeds even more rapidly.³ Reaction 14' proceeds with a rate of $k_{14'}$ [C₈H₁₈] = 1.5 × 10⁴ s⁻¹. Therefore, the decay slope of C₈H₁₇⁺ after 200 μ s is not affected by reactions 12, 14', and 15'. Thus, the slopes at 447, 483, and 509 K in Figure 10 can be attributed to reactions 24 and 13'. These reactions give the following expression for the concentration of C₈H₁₇⁺ after 200 μ s

$$\begin{bmatrix} C_8 H_{17}^+ \end{bmatrix} = \frac{k_{13'} [C_8 H_{18}] A}{k_{13'} [C_8 H_{18}] + k_{24}} + B \exp\{-(k_{13'} [C_8 H_{18}] + k_{24})t\}$$
(25)

where A is the total concentration of ions and B is a constant determined from the initial conditions. One can deduce values for k_{24} without explicit knowledge of A and B, as shown in the following discussion. Although various types of alkyl ions may participate in reaction 13', we used only one type rate constant $k_{13'}$ in eq 25 as an approximation. As can be seen in Figure 10, the C₈H₁₇⁺ intensities decreased more than one order of magnitude, finally reaching the steady-state concentration which corresponds to the first term of the right-hand side of eq 25. This means $k_{24} \gg k_{13'}$ [C₈H₁₈]. Therefore, the decay slopes at 447 and 483 K give the decay constants, k_{24} . At higher temperatures the decay slope approaches the decay slopes of NO⁺ and of $C_4H_9^+$ from reaction 11. (At high temperatures the $C_4H_9^+$ ions become the major product of reaction 11.) This is because reactions 11 and 13' become the main source of $C_8H_{17}^+$. In this case, the curve-fitting method can be used to obtain the k_{24} value. (This method was already explained to obtain the k_2 value.) The Arrhenius plots of k_{24} are given in Figure 7. The activation energy is calculated to be $E_{24} = 21 \pm 2$ kcal mol⁻¹ and the rate constant to be $k_{24} = 1.3 \times 10^{13} \exp(21000/RT)$ s⁻¹. Comparing k_{18} with k_{24} , it is found that the radical cations $C_8H_{18}^+$ are thermally less

stable than the corresponding alkyl cations $C_8H_{17}^+$. This instability comes from $E_{18} < E_{24}$. That is, the C-C bond of $C_8H_{18}^+$ would be weaker than that of $C_8H_{17}^+$ because of the presence of an unpaired σ electron.

Time-dependence curves for $C_4H_9^+$, $C_5H_{11}^+$, $C_6H_{13}^+$, and $C_8H_{17}^+$ in N₂-O₂(4100 ppm)-*n*-C₈H₁₈(2.0 ppm) at 483 K are shown in Figure 11. The C_4^+ ion intensity decreases at first and then increases. This can be explained by the existence of isomers. The initial C_4^+ ions from reaction 11 at high temperatures would have normal or secondary structures. The ions from reaction 24, however, would mainly have a tertiary structure; the tertiary ions will react with $n-C_8H_{18}$ much more slowly than the normal or secondary ions. The C_5^+ and C_6^+ alkyl ions with any structures seem to react very slowly with $n-C_8H_{18}$. Since the $n-C_8H_{18}$ content here is as low as 2 ppm, the occurrence of reactions between the fragment alkyl ions from reaction 24 and n-C₈H₁₈ is not observed in Figure 11. However, if one carries out experiment in 100% $n-C_8H_{18}$ vapor, these reactions would be observed. At that time, reaction 24 and 13' will make a chain mechanism. Indeed, Matsuoka et al. found that ionic chain reactions proceeded together with well-known radical chain reactions in the radiation-initiated thermal cracking of *n*-octane vapor.¹ They reported that the ionic chain products were C_3 - C_6 paraffins and C_3 - C_5 olefins, containing large quantities of branched products such as iso-C₄H₁₀, iso-C₄H₈, and iso- C_5H_{12} which were not formed by radical reactions. Formation of these branched products means that $n-C_8H_{17}^+$ ions from reaction 13' will isomerize before their thermal decomposition. The activation energy of the formation of the ionic chain products measured by Matsuoka et al. is about 22 kcal mol⁻¹ which agrees with $E_{24} = 21$ kcal mol⁻¹ measured here.

Conclusion

The $O_2^+ + C_n H_{2n+2}$ reaction prefers a charge-transfer channel to the more exothermic H⁻-transfer channel. The product alkane ions $C_n H_{2n+2}^+$ react with O_2 slowly producing $C_n H_{2n+1}^+$ and HO_2 . The olefinic ions $C_n H_{2n}^+$ also react with O_2 producing $C_n H_{2n-1}^+$ and HO_2 .

The $C_nH_{2n+2}^+$ ion is thermally less stable than the $C_nH_{2n+1}^+$ ion. This would be attributed to the presence of an unpaired electron in $C_nH_{2n+2}^+$ which weakens the C-C bond. Thermal decomposition of alkane ions (radical cations) produces olefinic ions (radical cations) and alkanes, and that of alkyl ions produces fragment alkyl ions and olefins. The thermal decomposition of $C_8H_{17}^+$ and the subsequent H⁻-transfer reaction between the product fragment alkyl ions and *n*- C_8H_{18} leads to an ionic chain mechanism in the radiation-initiated thermal cracking of *n*- C_8H_{18} vapor at temperatures above 500 K.

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Registry No. $C_2H_5^+$, 14936-94-8; C_2H_6 , 74-84-0; $C_2H_6^{*+}$, 34488-65-8; $C_3H_6^{*+}$, 34504-10-4; sec- $C_3H_7^+$, 19252-53-0; C_3H_8 , 74-98-6; $C_3H_8^{*+}$, 34479-70-4; $1-C_4H_8^{*+}$, 12544-69-3; $n-C_4H_{10}$, 106-97-8; $n-C_4H_{10}^{*+}$, 34479-72-6; $1-C_5H_{10}^{*+}$, 34467-40-8; $1-C_6H_{12}^{*+}$, 34467-41-9; $n-C_6H_{14}$, 110-54-3; $n-C_6H_{14}^{*+}$, 34478-20-1; $n-C_8H_{17}^+$, 53358-92-2; $n-C_8H_{18}$, 111-65-9; $n-C_8H_{18}^{*+}$, 62319-66-8; $(C_2H_5 \cdot H \cdot C_2H_5)^+$, 71500-08-8; O_2 , 7782-44-7; O^{*+} , 12185-07-8; NOO⁺, 14522-82-8; NO⁺, 14452-93-8.