Our measurements of k_7 provide a rationale for the results reported previously for the study of reaction 1 by Leu and Smith using the discharge-flow/resonance-fluorescence technique.⁷ In their work, OH was generated by reacting H with an excess of NO₂. The excess NO₂ removed CS_2OH (hence OH) quite efficiently due to the large reaction rate coefficient k_7 . If a reaction mechanism consisting of reactions 1f, 1r, and 7 is used in the steady-state approximation of CS_2OH , the observed effective rate coefficient for OH decay, k'_{obsd} , may be expressed as

$$k'_{\text{obsd}} \simeq k_7 [\text{NO}_2] K_c$$
 (25)

in which K_c is the equilibrium constant for reaction 1. With K_c = 8.7×10^{-18} cm³ molecule⁻¹ determined previously and $k_7 = 4.2$ \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, an estimated value [NO₂] \simeq 5 \times 10¹² molecules cm⁻³ employed by Leu and Smith gave $k'_{obsd} \simeq 2 \times$ 10^{-15} cm³ molecule⁻¹ s⁻¹, in agreement with their reported upper limit 3×10^{-15} cm³ molecule⁻¹ s⁻¹ at 298 K determined by observing the production rate of OCS. Some heterogeneous reactions of OH on the wall of the flow reactor apparently interfered the determination of the rate coefficient when the loss of OH was following instead; a value 2.9 \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ was determined.

In the chamber reaction of $OH + CS_2$ in the presence of O_2 by Barnes et al.,¹² NO₂ was present in both the photolytic and the "dark" experiments. With an estimate of $[NO_2] \simeq 25$ ppm and O_2 at 150 Torr, the effective rate of reaction 7 is ~16% that of k_{obsd} (for reaction 2) under synthetic air at 700 Torr. The contribution from reaction 7 to k_{obsd} would be greater if NO₂ could be somehow cycled back. Although the interference due to reaction 7 may not account for all of the discrepancies between the k_{obsd} values determined by Barnes et al. and those by Jones et al.^{10,11} and Hynes et al.,¹³ a correction on this effect is expected to reduce the k_{obsd} value reported by Barnes et al. to within the experimental uncertainties of other studies. However, this mechanism still cannot explain the greater k_{obsd} values observed by Becker et al. when H_2O_2 was used as a source of $OH^{.15}$ At lower partial pressure of O_2 , the interference due to reaction 7 became severe; this may explain why a $[NO_2]$ -dependent k_{obsd} was observed at less than 25 Torr of O_2 in the study of reaction 2 by Becker et al.¹⁵

In summary, the rate coefficients for the reactions of CS_2OH with O_2 , NO, and NO₂ have been determined to be k- $(CS_2OH + O_2) = (3.1 \pm 0.6) \times 10^{-14}, k(CS_2OH + NO) = (7.3 \pm 0.6) \times 10^{-14}, k(CS_2OH + 0.6) \times 10^{-14$ 1.8) \times 10⁻¹³, and $k(CS_2OH+NO_2) = (4.2 \pm 1.0) \times 10^{-11}$ molecule⁻¹ s⁻¹. All these reactions appear to be bimolecular and remove CS₂OH efficiently.

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Unimolecular Decomposition of the Neopentyl Radical

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The kinetics of the unimolecular decomposition of the neopentyl radical has been investigated. Experimentally, the decomposition was monitored in time-resolved experiments by using a heatable tubular reactor coupled to a photoionization mass spectrometer. The radicals were produced indirectly by pulsed excimer laser photolysis of CCl_4 (to produce $CCl_3 + Cl$) followed by the rapid reaction between the Cl atoms and neopentane to produce neo-C₅H₁₁ + HCl. Unimolecular rate constants were determined as a function of bath gas (He, N₂, and Ar), temperature (10 temperatures between 560 and 650 K), and bath gas density $((3-30) \times 10^{16} \text{ molecules cm}^{-3} \text{ (He) and } (6-12) \times 10^{16} (N_2, Ar))$. The data were fitted within the framework of RRKM theory by using a vibrational model. The high-pressure rate constant in the temperature range studied was determined to be $k(\text{neopenty}| \rightarrow \text{isobutene} + \text{CH}_3) = 10^{13.9\pm0.3} \exp(-30.9 \pm 1.0 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$. The average step sizes down for the bath gases used (adjusted parameters in the RRKM calculations) are comparable: 200 (He), 130 (N₂), and 140 (Ar) cm⁻¹ (all ± 60 cm⁻¹). The high-pressure-limit rate constant expression for the reverse reaction, nonterminal addition of CH₃ to isobutene, was obtained from thermochemical calculations by using the results of this study: $k(CH_3 + isobutene \rightarrow neopentyl)$ = $3.7 \times 10^{-13} \exp(-10.6 \text{ kcal mol}^{-1}/RT) \text{ cm}^3$ molecule⁻¹ s⁻¹. The Arrhenius parameters of this addition reaction indicate that nonterminal addition is inhibited relative to terminal addition mostly by a larger energy barrier to addition, as opposed to possible entropic effects.

Introduction

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The decomposition of alkyl radicals is an important part of the chemical kinetics of many high-temperature processes including the pyrolysis and oxidation of hydrocarbons.¹⁻³ For example, in hydrocarbon combustion, the competition between the unimolecular decomposition and the oxidation of the alkyl radicals is a key factor in determining many important properties of combustion, such as the nature and importance of products formed, sooting characteristics, and flame speeds. In addition, these de-

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compositions often result in the replacement of the relatively unreactive carbon-centered radical with the more reactive hydrogen atom (e.g., $i-C_3H_7 \rightarrow C_3H_6 + H$).

Existing experimental determinations of the alkyl-radical decomposition rate constants often show wide scatter.⁴ This is due

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in part to the fact that this information has been obtained largely from observations of the kinetic behavior of complex systems.

At the present time, for many of the alkyl radicals, the best unimolecular rate constant expressions are derived from kinetic data on the reverse reactions and thermodynamic properties of the reactants and products.⁵ These expressions have their own uncertainties and limitations. Generally they are derived from kinetic data obtained at much lower temperatures than those characteristic of pyrolysis or oxidation processes and under conditions which are near the high-pressure limit. Major extrapolations, in both the temperature and falloff characteristics of the unimolecular rate constant, are required to obtain rate constant expressions that can be used for modeling high-temperature chemical kinetics. Finally, uncertainties in the thermodynamic properties of the alkyl radicals persist^{6,7} as does an incomplete knowledge of the absolute values of the collisional efficiencies (and their temperature dependencies) needed to derive unimolecular decomposition rate constants that are valid at elevated temperatures.8,9

To gain new quantitative knowledge of the unimolecular decomposition of hydrocarbon radicals, we have begun to investigate the kinetics of these processes using an experimental approach that permits essential isolation of these reactions for quantitative study. Free-radical decays are monitored in time-resolved experiments. The current investigation is both an experimental and theoretical study of the decomposition of the neopentyl radical:

$$(CH_3)_3CCH_2 + (M) \rightarrow (CH_3)_2CCH_2 + CH_3 + (M) \quad (1)$$

First-order rate constants, $k_1(M,T)$, were obtained from the experiments and were fitted within the framework of RRKM theory. The theoretical calculations provided information on the collisional efficiencies of the bath gases and rate constant expressions for evaluating $k_1(M,T)$ for conditions other than those that were used in the current investigation.

The reverse reaction, reaction -1, nonterminal methyl addition, is only a minor reaction channel in the CH_3 + isobutene reaction compared to the preferred addition route, terminal addition. Since rate constants for such nonterminal additions have never been successfully measured, it has not been possible in the case of this or related reactions to accurately derive the decomposition rate constants from knowledge of the kinetics of the reverse reaction. Here, rate constants for the forward reaction, k_1 , are used to obtain kinetic parameters for the reverse reaction, the less-favored nonterminal methyl addition to the double bond of isobutene.

Prior studies of the thermal decomposition of the neopentyl radical are not in good agreement. Anderson and Benson¹⁰ have reported a rate constant of 1600 s⁻¹ for the unimolecular decomposition based on studies of the decomposition of neopentane at 753 K in the presence and absence of HCl. Assuming an A factor of 10^{13} s⁻¹, they obtain an activation energy of 34.5 kcal mol⁻¹. Furimsky and Laidler investigated the mercury-photosensitized decomposition of neopentane as a function of temperature (503-608 K) and report an Arrhenius expression for k_1 :¹¹

$$k_1 = 4.2 \times 10^{13} \exp(-29 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

This expression provides a value of k_1 at 753 K, which is about a factor of 60 higher than that reported by Anderson and Benson.

Some indication of the difficulty of nonterminal addition to olefins (and hence of the existence of a significant free energy barrier in reaction -1) can be derived from the study of Cvetanovic and Irwin, who investigated the kinetics of CH₃ addition to olefins.¹² From their results at 453 K, one finds $k_2/k_3 = 13.5$:

$$CH_3 + (CH_3)_2 CCH_2 \rightarrow products$$
 (2)

$$CH_1 + (CH_1)_2CC(CH_1)_2 \rightarrow \text{products}$$
 (3)

While the experiments with isobutene could not distinguish between terminal and nonterminal addition, it is very likely that the former is the predominant process in reaction 2 (resulting in the formation of the tert-amyl radical). Tedder and Walton have discussed the general observation¹³ that radical addition to unsaturated bonds occurs primarily at the least substituted site.

Tedder and Walton suggest further that this preference for addition to least-substituted sites is due largely to "steric effects". An interesting question is whether such steric effects appear as higher activation energies or lower A factors. The work of Cvetanovic and Irwin taken as a whole suggest the latter.¹²

Tsang has recommended unimolecular decomposition rate constant expressions (high-pressure limit) for reactions related to reaction 1 based partly on studies of the reverse reactions:¹⁴

$$n - C_3 H_7 \rightarrow C_2 H_4 + C H_3 \tag{4}$$

$$k_4 = 1.2 \times 10^{13} \exp(-30.3 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

$$i-C_4H_9 \to C_3H_6 + CH_3 \tag{5}$$

$$k_5 = 2 \times 10^{13} \exp(-29.9 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$

(Reactions 1, 4, and 5 form a homologous series of decomposition reactions, $R_1R_2CH_3CCH_2 \rightarrow R_1R_2CCH_2 + CH_3$, where R_1 and R_2 are either H or CH₃.) It is interesting to note that after taking into account the reaction path degeneracy, the rate constant expressions for reactions 4 and 5 are virtually the same. This unusually close agreement could be fortuitous. The rate constant expression for *n*-propyl radical is considered more reliable than that for the isobutyl radical. The former is based on the results of many earlier investigations which are in substantial agreement. The same cannot be said for the studies from which the expression for k_s was derived. The results of the current investigation are used to test the generality of this kinetic behavior.

Experimental Study

Apparatus and Procedure. The experiment consisted of rapidly producing the neopentyl radical at elevated temperatures by chemical reaction and subsequently monitoring its unimolecular decay in time-resolved experiments using photoionization mass spectrometry. Details of the experimental apparatus¹⁵ and most of the procedures used¹⁶ have been described before and so are only briefly reviewed here. Aspects of the present study that are unique are presented in detail.

The neopentyl radicals were produced by a two-step process: pulsed production of chlorine atoms by laser photolysis of CCl₄ followed by the rapid reaction of these atoms with neopentane to produce the radical:

$$\operatorname{CCl}_4 \xrightarrow{\operatorname{193 nm}} \operatorname{CCl}_3 + \operatorname{Cl}$$
 (6)

$$Cl + neo - C_5 H_{12} \rightarrow neo - C_5 H_{11} + HCl$$
(7)

Initial conditions (CCl₄ concentration and laser intensity) were selected to yield very low neo-C₅H₁₁ concentrations (typically in the range $(1-6) \times 10^{10}$ molecules cm⁻³)¹⁷ so that reactions between photolysis products (including the $C_5H_{11} + C_5H_{11}$ recombination reaction) had negligible rates compared to that of the unimolecular decomposition process under study. The *neo*- C_5H_{12} concentrations used were high enough to "convert" the Cl atoms to $neo-C_5H_{11}$ radicals (by reaction 7) in under 0.5 ms.

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Figure 1. Plot of k_1 vs 1000/T obtained from the set of experiments shown in Figure 2. [He] = 2.40×10^{17} atoms cm⁻³, [CCl₄] = 4.70×10^{12} molecules cm⁻³, [C₅H₁₂] = 7.84×10^{13} molecules cm⁻³. Inserts are the C₅H₁₁ and CH₃ ion signal profiles recorded at 600 K (solid circle on plot).

Pulsed, unfocused 193-nm radiation (≈ 5 Hz) from a Lambda Physik EMG 201 MSC excimer laser was directed along the axis of a heatable, uncoated quartz reactor (1.05-cm i.d.). Gas flowing through the tube at ≈ 4 m s⁻¹ contained CCl₄ (<0.1%), C₅H₁₂ (<0.3%), and an inert carrier gas (He, Ar, or N₂) in large excess (>99.6%). The flowing gas was completely replaced between laser pulses.

Gas was sampled through a hole (0.043-cm diameter or 0.025-cm diameter) located at the end of a nozzle in the side of the reactor and formed into a beam by a conical skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and mass selected. Temporal ion signal profiles were recorded on a multichannel scalar from a short time before each laser pulse to 18-20 ms following the pulse. Data from 500 to 32 000 repetitions of the experiment were accumulated before the data were analyzed.

The observed neopentyl radical decays were exponential in appearance under all experimental conditions. They were fit to a simple exponential function: $[C_5H_{11}]_t = [C_5H_{11}]_0 e^{-kt}$; see the insert in Figure 1. From 300 to 450 K the C_5H_{11} exponential decay constants (k) were essentially independent of temperature for any initial gas density used. Above 450 K the decay constant increased, first slowly and then rapidly with rising temperature (see Figure 2). This dramatically enhanced decay at elevated temperatures is interpreted as due solely to the increasing importance of C_5H_{11} thermal decomposition.

The C_5H_{11} decay constants were analyzed assuming that the *neo*- C_5H_{11} radicals were consumed by two elementary reactions:

$$neo-C_5H_{11} \rightarrow CH_3 + C_4H_8 \tag{1}$$

$$neo-C_5H_{11} \rightarrow heterogeneous loss$$
 (8)

It is the relatively temperature-independent heterogeneous C_5H_{11}



Figure 2. Plot of k' vs 1000/T for a set of experiments to determine $k_1(T)$ at a fixed density of the bath gas helium. [He] = 2.40×10^{17} atoms cm⁻³; [CCl₄] = 4.70×10^{12} molecules cm⁻³; [C₅H₁₂] = 7.84×10^{13} molecules cm⁻³. Measured values of $k_8 = 14$ s⁻¹ (dark circles) and extrapolated values (dotted line) are indicated.

loss (reaction 8) that is observed at low temperatures and the sum of the two loss processes that is observed above 450 K, $k' = k_8 + k_1$.

Sets of experiments were conducted to determine k_1 as a function of temperature at different fixed gas densities. The C_5H_{11} exponential decay constant, k', was measured as a function of temperature (typically from 300 to 650 K), keeping the concentrations of all gases constant (the bath gas, C_5H_{12} , and CCl_4). Calculations of k_1 from measurements of k' require knowledge of k_8 above 450 K. While k_8 (at the fixed total gas density) was directly determined between 300 and 450 K, it could not be measured above this temperature due to the additional loss of *neo*-C₅H₁₁ by unimolecular decomposition. Below 450 K, k_8 was directly determined (because $k' = k_8$) where this constant was found to be essentially temperature independent (see Figure 2). Values of k_8 above 450 K needed for the data analysis were obtained by extrapolation, assuming k_8 retains this temperature independence up to highest temperature of this investigation, 650 K. The determinations of k_1 from one such set of experiments are plotted in Figure 1.

To minimize possible errors in the determinations of k_1 caused by the assumed continued temperature independence of k_8 above 450 K, experiments to obtain k_1 were conducted only at temperatures sufficiently high to ensure that $k' > 3k_8$. It was this criterion that established the lowest temperature used to determine k_1 in each set of experiments. The highest temperature used at each total gas density was determined by the fact that decay constants above 600 s⁻¹ cannot be measured accurately.¹⁸

Similar sets of experiments were conducted at other gas densities and using three different bath gases (Ar, He, and N₂) providing, in the end, sections of the unimolecular falloff curves $(k_1 vs [M])$ at different temperatures for each of the bath gases used.

Estimated uncertainties in the k_1 determinations vary from $\pm 15\%$ in the middle of the temperature range to $\pm 25\%$ at the extreme temperatures used. The higher uncertainty at the lowest

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Log ([M]/ cm⁻³)

Figure 3. Plot of log k_1 vs log [M] for experiments conducted at 10 temperatures using helium as the bath gas. Lines are the best RRKM fits of the data (see text).

temperatures is due to the significant correction for heterogeneous loss of the radical needed to obtain k_1 from the measured *neo*- C_5H_{11} decay constants. At the highest temperature, the decay constant is rapid, near the limit of what can be measured accurately by our experimental technique.

Before these experiments were begun, a series of tests were performed to ensure that k' depended only on T and [M] as predicted by the mechanism used for radical loss. At 620 K and at a fixed total gas density, [He] = 3×10^{16} cm⁻³, k' did not depend on the *neo*- C_5H_{12} concentration (which was varied by a factor of 10). This indicates that there was no significant reaction between $neo-C_5H_{11}$ and neopentane under our experimental conditions. The decay constant was also independent of [CCl₄] (which was varied by a factor of 4 to increase Cl atom and CCl₃ production by photolysis and also the initial $neo-C_5H_{11}$ concentration), which indicates that reactions between $neo-C_5H_{11}$ and CCl_4 as well as radical-radical reactions (such as $CCl_3 + C_5H_{11}$ and $C_5H_{11} + C_5H_{11}$) were also unimportant. The absence of any interference by radical-radical reactions was also confirmed by reducing the laser intensity by a factor of 2, which, while reducing the initial C_5H_{11} concentration by this factor, resulted in no change in the measured value of k'. These results all support the belief that the *neo*- C_5H_{11} decomposition mechanism used to interpret the data is complete. The independence of k' on $[CCl_4]$ and $[C_5H_{12}]$ also indicates that the carrier gas (Ar, He, or N₂), which is in great excess (>99.6%), is the important bath gas. Abbreviated versions of these tests were repeated periodically under other experimental conditions, and the same results were obtained.

Photoionization in the mass spectrometer is provided by resonance lamps. Three ionization energies were used in this investigation. An argon lamp (11.6, 11.8 eV) was used to photoionize CCl_4 , a hydrogen lamp (10.2 eV) to photoionize CH_3 and C_4H_8 , and a chlorine lamp (8.9–9.1 eV) to photoionize C_5H_{11} .

The gases used were obtained from Aldrich (CCl₄, 99.9%) and Matheson (2,2-dimethylpropane, 99%; He, 99.995%; Ar, 99.998%; N₂, 99.998%). CCl₄ and C₅H₁₂ were purified by freeze-pumpthaw cycles prior to use. The other gases were used as provided.

Experimental Results. The C_5H_{11} thermal decomposition rate constant, k_1 , was determined as a function of bath-gas density, the identity of the bath gas, and temperature. Ten temperatures in the range 560-650 K were used. Over a 10-fold range of helium



Figure 4. Plot of log k_1 vs log [M] for experiments conducted at seven or eight temperatures with N₂ and Ar as the bath gases. Lines are the best RRKM fits of the data (see text).

concentrations was covered $((3-30) \times 10^{16} \text{ atoms cm}^{-3})$ as was a 2-fold range of argon and nitrogen concentrations $((6-12) \times 10^{16} \text{ molecules cm}^{-3})$ when they were used as the bath gases. The rate constant is in the falloff region under these experimental conditions. The conditions and results of all experiments are given in Table I. The results for the helium experiments are plotted in Figure 3, and those in which argon and nitrogen were used as the bath gases are shown in Figure 4.

The products of the neopentyl radical decomposition (CH₃ and C₄H₈) were also detected and recorded. The C₄H₈ ion signal was obscured by photoionization fragmentation of the neopentane at mass 56. However, the signal was qualitatively observed to rise at a rate similar to the C₅H₁₁ decay. The CH₃ ion signal was observed to rise and then slowly decay (probably due to heterogeneous wall loss). A small set of experiments was conducted to observe the methyl radical temporal behavior. Its exponential growth constant was within ±10% of the neopentyl radical decay constant (see insert in Figure 1 for a typical example). These experiments confirm the known radical decomposition mechanism and indicate that the products of the decomposition did not subsequently react in a manner that interfered with the essential isolation of the *neo*-C₅H₁₁ decomposition process.

Data Analysis

From the shape of the falloff curves in Figures 3 and 4, it is apparent that the rate constants for neopentyl decomposition are fairly close to the high-pressure limit. RRKM calculations¹⁹ have been used to extrapolate the most extensive set of data, that with helium as the collider, to determine the limiting high-pressure rate constants. It is well-known that the key determinants for RRKM calculations of unimolecular rate constants are the high-pressure rate expression (A factor and activation energy) and the step size down on a per collision basis, where the latter has been derived from the collision efficiency on the basis of Troe's treatment of weak collision effects.²⁰ Thus details of the transition-state models are relatively unimportant. Since radical additions to olefins have activation energies, the position of the transition state along the

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TABLE I: Conditions and Results of Experiments To Measure the Unimolecular Rate Constant (k_1) for the Thermal Decomposition of Neopentyl Radicals

	10 ⁻¹⁶ [M],	10 ⁻¹² [CCl ₄],	10 ⁻¹³ [C ₅ H ₁₂],				10 ⁻¹⁶ [M],	10 ⁻¹² [CCl ₄],	$10^{-13}[C_5H_{12}],$		
	molecules	molecules	molecules	k ₈ ,	k ₁ , ^b		molecules	molecules	molecules	k ₈ ,	k1,8
<i>T</i> ,ª K	cm ⁻³	cm ⁻³	cm ⁻³	s ⁻¹	s ⁻¹	<i>T</i> ,ª K	cm ⁻³	cm ⁻³	cm ⁻³	s ⁻¹	s ⁻¹
M = Helium											
560	6.01	5.68	5.82	17.4	35.3	600 ^{c,d}	24.0	4.70	7.84	19.0	256
560°	12.0	5.67	5.55	17.1	42.4	600°	30.0	5.52	6.42	19.7	270
560°	18.0	4.93	5.78	25.5	45.3	610	3.00	29.5	9.17	34.7	175
560°	24.0	4.70	7.84	19.0	49.1	610	3.00	6.43	6.28	48.8	165
560°	30.0	5.52	6.42	19.7	46.4	610	4.49	6.32	6.45	31.7	187
570	6.00	19.2	19.3	27.7	54.0	610	6.00	19.2	19.3	27.7	236
570°	6.01	5.68	5.82	17.4	53.4	610°	6.00	5.36	5.99	21.5	235
570°	12.0	5.67	5.55	17.1	62.7	610°	12.0	5.67	5.55	17.1	314
570°	18.0	4.93	5.78	25.5	69.0	610 ^c	18.0	4.93	5.78	25.5	341
570°	24.0	4.70	7.84	19.0	75.8	610 ^c	24.0	4.70	7.84	19.0	364
570°	30.0	5.52	6.42	19.7	75.6	610 ^c	30.0	5.52	6.42	19.7	398
580	3.00	29.5	9.17	39.4	75.8	620	3.00	29.5	9.17	34.7	226
580	4.49	6.36	6.52	31.9	66.0	620	3.00	6.43	6.28	48.8	222
580	6.00	19.2	19.3	27.7	78.6	620	4.49	6.73	6.61	31.9	260
580°	6.01	5.68	5.82	17.4	81.6	620	6.00	19.2	19.3	27.7	310
580°	12.0	5.67	5.55	17.1	96.7	620°	6.00	5.36	5.99	21.5	351
580°	18.0	4.93	5.78	25.5	108	620°	12.0	5.67	5.55	17.1	417
580	24.0	4.70	7.84	19.0	115	620	18.0	5.11	5.77	41.2	458
580	30.0	5.52	6.42	19.7	111	620°	24.0	4.70	7.84	19.0	557
590	3.00	29.5	9.17	39.4	102	620	30.0	5.46	6.66	25.5	527
590	4.49	6.32	0.45	31.7	8/.3	630	3.00	29.5	9.17	34./	302
590	6.00	19.2	19.3	27.7	113	630	3.00	0.43	0.28	48.8	304
590	0.01	5.08	5.82	17.4	110	630	4.49	0./3	0.01	31.9	339
5000	12.0	3.07	5.55	17.1	143	630	6.00	19.2	19.5	21.7	429
5000	18.0	4.93	3.70 7 PA	23.5	159	630	0.00	5.50	5.99	21.5	4/0
590	24.0	4.70	6 4 2	19.0	104	640	12.0	3.60	5.73	247	200
600	3 00	29.52	0.42	20 /	125	640	3.00	29.J 6 10	6.17	J4./	370
600	3.00	6 43	6.28	19.4	119	640	3.00 A 40	6.73	6.61	310	AA7
600	4 49	6 3 2	6.45	317	134	640	6.00	19.7	10.3	27.7	562
600	6.00	19.2	193	27.7	170	650	3.00	29.5	9.17	347	522
600	6.00	5 36	5 99	21.5	163	650	3.00	610	6.23	48.8	504
600	12.0	5.50	5 55	171	209	650	4 4 9	6 73	6 61	31.9	557
600	18.0	4.93	5.78	25.5	233	000		0.75	0.01	51.7	551
	1010		0110	2010	200						
					M = N	itrogen					
580	12.0	34.3	13.1	33.1	65.0	620	6.00	22.1	10.1	30.4	210
590	6.00	22.1	10.1	30.4	65.8	620	12.0	31.9	13.4	30.9	287
590	12.0	34.3	13.1	33.1	91.7	630	6.00	22.1	10.1	30.4	282
600	6.00	22.1	10.1	30.4	104	630	12.0	31.9	13.4	30.9	442
600	12.0	34.3	13.1	33.1	130	640	6.00	22.1	10.1	30.4	364
610	6.00	22.1	10.1	30.4	148	640	12.0	31.9	13.4	30.9	552
610	12.0	31.9	13.4	30.9	215	650	6.00	22.1	10.1	30.4	479
M = Argon											
590	6.00	37.4	6.90	35.3	72.5	610	12.0	37.3	6.93	44.6	200
590	6.00	14.2	5.92	39.6	71.2	620	6.00	37.4	6.90	35.3	210
590	6.00	35.6	5.92	39.8	71.3	620	12.0	37.3	6.93	44.6	262
590	6.00	35.6	10.3	36.0	71.8	630	6.00	37.4	6.90	35.3	271
590	12.0	37.3	6.93	44.6	87.9	630	12.0	37.3	6.93	44.6	344
600	6.00	37.4	6.90	35.3	114	640	6.00	37.4	6.90	35.3	361
600	12.0	37.3	6.93	44.6	132	640	12.0	37.3	6.93	44.6	475
610	6.00	37.4	6.90	35.3	152	650	6.00	37.4	6.90	35.3	447

^a Temperature variation: ± 1 for T < 500 K; ± 2 for T = 550-650 K. ${}^{b}k_{1} = k' - k_{8}$; estimated uncertainty discussed in text. ^c Experiments performed using reactor with 0.025-cm-diameter leak. All other experiments performed using reactor with 0.043-cm-diameter leak. ^d Experiment shown in Figure 1.

reaction coordinate is clearly defined. Hence a simple vibrator model was used in these RRKM calculations to obtain the high-pressure limit rate constants.

Values of $k_1(M,T)$ were calculated by using the following procedure. A predetermined Arrhenius A factor for the highpressure limit rate constant was obtained through selection of appropriate vibrational frequencies of the transition state. Then the other two "unknown" parameters (the high-pressure limit activation energy and the step size down) were varied to obtain the best agreement between measured and calculated rate constants. The procedure was repeated to search for the optimum agreement between calculation and experiment. First, a higher or lower Arrhenius A factor was generated by changing the vibration frequencies of the transition state. Then the two remaining parameters were again optimized. The three adjusted parameters are not unique. Changes in one of the fitted parameters could partially compensate for forced changes in another. However, the relatively large range of conditions used and the large body of data to be fitted minimizes this effect. To obtain an estimate of the uncertainty in the adjusted reaction parameters, sets of calculations were conducted in which the A factor was changed by successive factors of 2. For each A factor, the remaining parameters, the energy barrier and the step size down, were found that generated the best possible fit to the data. It was apparent that a change in the A factor of the high-pressure limit by a factor of 2 from the optimum value resulted in a global fit of theory to experiment that was slightly but noticeably poorer after the energy barrier and step size down were reoptimized. Changing the A factor by this amount results in a change in the energy barrier of less than 1 kcal mol⁻¹ and

TABLE II: Molecular and Thermodynamic Properties of the Neopentyl Radical

	<i>C</i> _p °,	S°,	-(<i>G</i> _T °	$-H_0^{\circ})/T$
temp, K	cal/(mol·K)	cal/(mol·K) cal/	(mol·K)
200	22.31	73.20	-	58.68
298.16	28.83	83.34	-	65.17
300	28.95	83.52	-	65.28
400	35.45	92.73	_	71.00
500	41.43	101.30	-	76.22
600	46.75	109.33	-	81.09
700	51.42	116.90	-	85.67
800	55.52	124.03	_	90.03
900	59.11	130.78	_	94.19
1000	62.24	137.18	-	98.16
	$H - H_0$,	$\Delta H_{\rm f}^{\rm o}$,	$\Delta G_{\rm f}^{\circ}$,	log K _p ,
temp, K	cal/mol	cal/mol	cal/mol	atm
200	2904.7	10668.3	28526.4	-31.17
298.16	5417.4	8735.5	37504.6	-27.49
300	5470.5	8700.0	37680.5	-27.45
400	8691.3	6863.6	47489.2	-25.94
500	12540.6	5280.1	57731.5	-25.23
600	16943.6	3947.2	68260.4	-24.86
700	21561.9	2885.9	79003.1	-24.66
800	27196.8	2039.3	89860.8	-24.55
900	32932.8	1428.1	100832.8	-24.48
1000	39018.1	1038.0	111868.3	-24.45
vibr freq:	2950 (7), 2913	3 (1), 2900 (3), 1470 (8),	1370 (2),
1360 (1), 1250 (2), 11	50 (1), 950 (3	3), 925 (3),	733 (1),
560 (1)	, 414 (3), 335	(2)		

product of the moments of inertia: $6.7 \times 10^{-114} \text{ (g cm}^2)^3$ symmetry no.: 2

moment of inertia: methylene rotor (free), 3×10^{-40} g cm²; sym no. = 2

moment of inertia: methyl rotor (hindered, 4 kcal mol⁻¹), 5×10^{-40} g cm²; sym no. = 3

heat of formation at 300 K: 8.7 kcal mol⁻¹

TABLE III: Parameters Used in Vibrator Model Transition-State Calculations

vibr freq (degeneracy) (a) molecule: 200 (3), 350 (2), 400 (3), 700, 900 (3), 1000 (5), 1250 (2), 1350, 1400 (3), 1450 (6), 1500 (2), 2950 (11), 1 free methyl rotor⁴ (b) transition state: 150 (5), 300, 350, 400, 700, 900 (2), 1000 (5), 1250 (2), 1350, 1400 (3), 1450 (6), 1500 (2), 2950 (11) reaction path degeneracy = 3

 $^{\rm a}$ For calculational convenience hindered rotors are treated as 200- $\rm cm^{-1}$ vibrations.

the step size down changes by $50-70 \text{ cm}^{-1}$. We conclude that these changes are measures of the uncertainties in the fitted parameters.

The ultimate best global fit of the calculations to the measured values of $k_1(M,T)$ are shown as the lines through the data in Figures 3 and 4. The neopentyl radical molecular parameters for this case (and the associated thermodynamic properties calculated from these parameters) are given in Table II. The reaction transition-state properties are presented in Table III.

The "best" high-pressure rate expression for the temperature range 560-640 K in Arrhenius form is

$$k_1 = 10^{13.9 \pm 0.5} \exp(-30.9 \pm 1.0 \text{ kcal mol}^{-1}/RT) \text{ s}^{-1}$$
 (I)

The final step size down for this temperature range is 200 ± 60 cm⁻¹ (He).

With this high-pressure rate expression obtained from the extensive set of experiments with helium as the collider, the unimolecular rate constants determined by using argon and nitrogen were also fitted by finding the best value for the step size down that would reproduce the experimental rate constant measurements. The best theoretical rate constants obtained are shown in Figure 4. These have been obtained by using step sizes down of 130 ± 60 and 140 ± 60 cm⁻¹ for N₂ and Ar, respectively.

Significant fractional uncertainties in the step size down exist (30-50%) as a result of the relative insensitivity of the reported

experiments to this parameter. The experiments were all conducted not far from the high-pressure limit. Hence caution is advised in extrapolating the unimolecular rate constants to much lower pressures where falloff effects are far more pronounced.

Discussion

Agreement between Experimental Results and Theoretical Fits of k_1 . It is apparent from the measured and calculated values of k_1 displayed in Figures 3 and 4 that the RRKM theory provides an excellent formalism for fitting the temperature and density dependencies of these unimolecular rate constants. The RRKM calculations for He involved adjusting three parameters. The data fitted include 56 rate constants obtained at 10 different temperatures and span a 10-fold range of pressure. In the RRKM calculations of k_1 for the other two bath gases, N₂ and Ar, only the collision parameter was varied since the high-pressure-limit values of k_1 were regarded as established by the fitted helium experiments.

The only hint of a systematic deviation between theory and experiment is in the highest temperature helium experiments where the experimental values appear systematically below the theoretical values. The deviation is within the experimental uncertainty and does not appear in the nitrogen or the argon experiments.

Comparison with Results of Prior Determinations of k_1 . There have been no prior direct determinations of k_1 . Earlier values come from indirect investigations that combined measurements of stable product yields from complex reactions with presumed knowledge of the reaction mechanisms, Arrhenius parameters of other elementary reactions besides reaction 1, and in one case a data extrapolation. The value of k_1 at 762 K reported by Anderson and Benson¹⁰ (2 × 10³ s⁻¹) is not in good agreement with the current results. Our Arrhenius expression for k_1 yields a value of 1.0×10^5 s⁻¹ at this temperature, a factor of 50 higher.

The experiments of Furimsky and Laidler¹¹ provide values of k_1 as a function of temperature (503-608 K) and pressure (10-280 Torr). At 600 K, their high-pressure rate constant expression yields a value of k_1 that is 1.6 times higher than our own at this temperature. Considering the differences in experimental approaches, this agreement is satisfactory. However, the authors report anomalous pressure dependencies of k_1 such as neopentane being a less efficient collision partner than helium. Clearly there are mechanistic artifacts in the lower pressure results of Furimsky and Laidler. Hence comparisons of numerical values are not meaningful at reduced pressures.

Similarities in High-Pressure Limit Rate Constants of Reactions 1, 4, and 5. As was mentioned in the Introduction, reactions 1, 4, and 5 can be viewed as an homologous series of radical unimolecular decomposition reactions. Each reaction involves the loss of a CH₃ group from the β position of a methyl-substituted ethyl radical: (CH₃)CH₂CH₂, (CH₃)₂CHCH₂, and (CH₃)₃CCH₂. Within the limit of uncertainty of the Arrhenius parameters and the activation energies, there is unusual similarity in the kinetic parameters of these reactions. The Arrhenius A factors (which are all uncertain by a factor of 2) increase with methyl substitution to values reasonably close to those expected simply from the degeneracy of the reaction path: 1.2×10^{13} , 2×10^{13} , and 7.8 $\times 10^{13}$ s⁻¹. The activation energies (uncertain by 1 kcal mol⁻¹) are all essentially the same: 30.3, 29.9, and 30.9 kcal mol⁻¹. Finally, at 600 K, the ratios of rate constants (per methyl group) for the three free-radical unimolecular decomposition reactions (n-propyl, isobutyl, and neopentyl) are 1:1.2:1.3. These numbers are closer than the ratios of A factors (per methyl group), 1:0.8:2.1, indicating perhaps a greater closeness (on a per methyl group basis) of the free energy of activation than of the entropies of activation.

A comparable similarity does not exist among the unimolecular decompositions of the alkanes where, as one goes from propane to isobutane and neopentane, there is a considerable increase in the rate constants for CH_3 loss (on a per carbon-carbon bond basis),²¹ one which can be associated with the weakening of the

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C-CH₃ bond in the alkane with increasing methyl radical substitution. The experimental results obtained on the unimolecular decomposition of the alkyl radicals discussed above indicate that there is no comparable weakening of the C-CH₃ bonds with increasing CH₃ substitution. This unexpected behavior of the radicals may be caused by compensating factors associated with the fact that decomposition involves the simultaneous cleavage of the C-CH₃ bond and the formation of the π bond in the product olefin.

Kinetics of Nonterminal Addition of CH₃ to Isobutene. Reaction -1, the reverse of that studied, involves the addition of a methyl radical at the most highly substituted carbon in isobutene. The rate constant for this reaction can be obtained from the rate constant expression for reaction 1 and the equilibrium constant for the decomposition process. The equilibrium constant was calculated by using the known thermodynamic properties of isobutene and the methyl radical and calculated properties of the neopentyl radical. The heat of formation of the neopentyl radical was obtained assuming that the primary C-H bond energy in neopentane is the same as in ethane, 100.5 kcal mol^{-1,22} Heat capacities and entropies of the radical were calculated from standard statistical thermodynamic relations. Frequency assignments were made following the general procedures outlined by Benson.²³ The properties of the radical and its thermochemical properties are given in Table II.

As is generally the case when determining thermochemical properties of larger free radicals, a major uncertainty in the values calculated is associated with the barriers selected for the internal rotations. In our calculations the methylene group is treated as a free rotor and the methyl-group rotation has a barrier of 4 kcal mol^{-1} . This leads to a rate constant expression for nonterminal methyl radical addition to isobutene of

$$k_{-1} =$$

$$3.7 \times 10^{-13} \exp(-10.6 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(II)

To obtain an indication of the uncertainty of the Arrhenius parameters caused by the selection of the C-CH₃ rotation barrier, calculations were also performed reducing the barrier to 2 kcal mol⁻¹. This change simulates a significant and probably unrealistic looseness in the neopentyl radical. The resulting Arrhenius expression for k_{-1} is

$$k_{-1} =$$

 $8.5 \times 10^{-13} \exp(-10.4 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (III)

At the temperatures of our investigation, the latter expression for k_{-1} yields values a factor 2.6 larger than the former.

Cvetanovic and Irwin¹² obtained Arrhenius parameters for the total addition rate constant for the CH_3 + isobutene reaction: $k(CH_3 + isobutene) =$

$$2.3 \times 10^{-13} \exp(-6.9 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

As the total addition rate constant must be for addition that is essentially exclusively at the terminal position, rate constant expressions are now in hand for both the terminal (IV) and nonterminal addition (II). While there are uncertainties in both expressions, comparisons are worth noting. At a typical temperature of the Cvetanovic and Irwin study, 400 K, these rate constant expressions indicate that the terminal addition is 63 times faster than the nonterminal addition. The selectivity is due mostly to the different activation energies for addition at the two sites (the Arrhenius A factors are nearly the same for the two addition processes). This implies that if temperature were increased, nonterminal addition will become increasingly more important. The same conclusion was reached for the case of hydrogen addition to isobutene.²⁴ Feld and Szwarc²⁵ noted that A factors for *terminal* addition were all very similar. Our observation that the A factors for terminal and nonterminal addition are also the same (at least in the case of isobutene) extends this generality to include both addition sites. Actually this broadened generality follows from our earlier observation, discussed above, that the A factors (per C-CH₃ bond) for the decomposition of the three substituted ethanes are essentially the same.

Extension of Experimental Results and Energy-Transfer Effects. As an aid to those who require rate constants for neopentyl radical decomposition under conditions outside the range of conditions used in this investigation, we provide in Table IV information necessary for the determination of their values. In an earlier section we pointed out that three parameters, the activation energy, A factor, and the step size down, are all that is needed for such determinations.

The energy-transfer parameter, the step size down, varies with the collisional partner and with temperature. It is impossible to provide rate constant expressions for all possible bath gases and the likely temperature dependencies of the step size down. Therefore information is provided in Table IV in the form of two parts that can be used with any preferred step size. Table IVA contains the results of RRKM calculation assuming strong collisions with the molecule itself as the collision partner. Table IVB contains collision efficiencies as a function of step size down and temperature. This information has been obtained based on the work of Gilbert et al.²⁶

To determine a rate constant at a particular temperature, one selects an appropriate step size and obtains the collision efficiency on a per collision basis from the data in Table IVB. The total collisional efficiency is then determined by multiplying this quantity by the ratio of the actual number of the kinetic theory collisions with the specific partner and the strong collider (neopentyl). The relevant properties for the neopentyl radical are given in Table IVC. The properties for other collisional partners can be found in standard texts.²⁷ Multiplication of the total collisional efficiency with the reaction pressure leads to an equivalent strong collision pressure. The appropriate k/k(inf) value can then be read from Table IVA. Some examples of the calculational procedure can be found in an earlier reference.¹⁴

The pressure dependence determined in these studies provides a measure of the influence of energy transfer in unimolecular reactions. The step size down that we report is dependent on the accuracy of the rate expression and the particular model for energy transfer. In the present case our treatment is based on the work of $Troe^{20}$ and involves an exponential model for the transition probabilities for deactivation. Other more elaborate approaches involving the direct solution of the master equation can also be used and will lead to somewhat different numbers.⁹ The present approach is employed because of its use to fit a great deal of similar data on hydrocarbons and the generalizations so obtained may have some validity on a purely comparative basis.

In the present study we are fairly close to the high-pressure limit; thus the uncertainty in the step size down, $\pm 60 \text{ cm}^{-1}$, is quite large. Nevertheless, we have found that the value for helium in isopropyl radical decomposition²⁸ is very close to this value. It is also fairly close to the data for H + CH₃ and CH₃ + CH₃ in this temperature range.²¹

The temperature range covered in this study is not frequently used for studies of unimolecular decomposition of hydrocarbons. Information on the step size down comes from studies of the unimolecular decomposition of stable hydrocarbon molecules in the 1000-2000 K range. The reverse hydrocarbon formation processes are typically investigated near ambient temperature. From the high-temperature shock tube studies with argon as the

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TABLE IV: Tabulated Information To Calculate Rate Constants for Neopentyl Decomposition as a Function of Temperature and Pressure

(A) Log (k/k(inf)) for the Reaction neo-C₅H₁₁ \rightarrow i-C₄H₈ + CH₃ as a Function of Temperature and Pressure Assuming Strong Collisions

log	Т, К										
density	400	500	600	700	800	900	1000	1100	1200	1300	1400
15	-0.11	-0.27	-0.51	-0.80	-1.14	-1.49	-1.85	-2.20	-2.55	-2.87	-3.17
15.5	-0.05	-0.16	-0.33	-0.56	0.84	-1.15	-1.47	-1.79	-2.11	-2.41	-2.70
16	-0.02	-0.08	-0.19	-0.37	-0.59	-0.85	-1.12	-1.41	-1.69	-1.97	-2.24
16.5	-0.01	-0.04	-0.10	-0.22	-0.38	-0.59	-0.82	-1.06	-1.31	-1.56	-1.80
17		-0.01	-0.05	-0.12	-0.23	-0.38	-0.55	-0.75	-0.96	-1.17	-1.39
17.5		-0.01	-0.02	-0.06	-0.12	-0.22	-0.35	-0.49	-0.66	-0.83	-1.01
18			-0.01	-0.02	-0.06	-0.11	-0.19	-0.29	-0.41	-0.54	-0.68
18.5				-0.01	-0.02	-0.05	-0.09	-0.15	-0.23	-0.32	-0.42
19					-0.01	-0.02	-0.04	-0.07	-0.11	-0.16	-0.23
19.5						-0.01	-0.01	-0.03	-0.05	-0.07	-0.11
20								-0.01	-0.02	-0.03	-0.04

(D) Comaton Enterency	as a remember of rempetature and step	DILO DOWN IOI INO RODUNIO	1 1100 031111	, 04118 . 0113 . 101
		sten size cm ⁻¹		

	step size, cili						
<i>Т</i> , К	50	100	200	400	800		
 400	9.0 × 10 ⁻³	3.0×10^{-2}	8.7 × 10 ⁻²	2.1 × 10 ⁻¹	3.9 × 10 ⁻¹		
500	4.6×10^{-3}	1.6×10^{-2}	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}		
600	2.4×10^{-3}	8.6×10^{-3}	2.9×10^{-2}	8.4×10^{-2}	2.0×10^{-1}		
700	1.3×10^{-3}	4.9×10^{-3}	1.7×10^{-2}	5.4×10^{-2}	1.4×10^{-1}		
800	8.5×10^{-4}	3.2×10^{-3}	1.2×10^{-2}	3.8×10^{-2}	1.1×10^{-1}		
900	6.7 × 10 ⁻⁴	2.6×10^{-3}	9.4×10^{-3}	3.2×10^{-2}	9.7×10^{-2}		
1000	6.2×10^{-4}	2.4×10^{-3}	8.9 × 10 ⁻³	3.1×10^{-2}	9.7 × 10 ^{−2}		
1100	6.4×10^{-4}	2.5×10^{-3}	9.3 × 10 ⁻³	3.3×10^{-2}	1.1×10^{-1}		
1200	7.1×10^{-4}	2.8×10^{-3}	1.0×10^{-2}	3.7×10^{-2}	1.2×10^{-1}		
1300	8.2×10^{-4}	3.2×10^{-3}	1.2×10^{-2}	4.3×10^{-2}	1.4×10^{-1}		
1400	9.5 × 10 ⁻⁴	3.7×10^{-3}	1.4×10^{-2}	4.9×10^{-2}	1.6×10^{-1}		

(C) Transport Properties for Neopentyl Radical (Results Based on Neopentane)

collisional diameter 5.66 Å

Lennard-Jones well depth 368 K

(D) Recommended log k/k(inf) Values for the Reaction neo-C₅H₁₁ \rightarrow i-C₄H₈ + CH₃ in the Presence of N₂ at 0.1, 1, and 10 atm

 $\log [k/k(inf); 0.1 \text{ atm}, N_2] = -6.2153 + 7.6395 \times 10^3/T - 3.1073 \times 10^6/T^2 + 4.7411 \times 10^8/T^3$ $\log [k/k(inf); 1.0 \text{ atm}, N_2] = -4.6541 + 6.6330 \times 10^3/T - 3.1330 \times 10^6/T^2 + 4.8958 \times 10^8/T^3$

 $\log [k/k(inf); 10.0 \text{ atm}, N_2] = -2.6882 + 4.2668 \times 10^3/T - 2.2178 \times 10^6/T^2 + 3.7661 \times 10^8/T^3$

third body, one obtains step sizes down that are factors of 3-5 larger than that obtained here. At ambient conditions the numbers were factors of 2-3 smaller. It is very tempting to assume that for hydrocarbons there is a roughly a linear dependence of the step size down on temperature. On the basis of this assumption and using the experimentally determined step size down of 130 cm^{-1} for N₂, we give in Table IVD a relationship for k/k(inf) for pressures of 0.1, 1.0, and 10 atm. Due to the uncertainties discussed here, there may be significant errors as one departs very far from the experimental conditions. We also note that for a non-hydrocarbon compound, CH₃NC,²⁹ the falloff data for isomerization in helium is best fitted with a step size down of 450 cm⁻¹. Fortunately, it is suspected that for most applications where kinetics may be important, the unimolecular decomposition processes are near the high-pressure limit.

Summarv

First-order rate constants for the unimolecular decomposition of the neopentyl radical, $k_1(M,T)$, were measured as a function of temperature and pressure. The Arrhenius parameters for the high-pressure limit rate constant were obtained by fitting calculated rate constants (RRKM theory, vibrator model) to the measured values. The falloff behavior yielded values of the average step size down near 600 K for the three bath gases used, He, Ar, and N_2 . Thermochemical calculations using the high-pressure values of k_1 yielded the rate constant for the reverse reaction, nonterminal addition of CH₃ to isobutene. Comparison of the Arrhenius parameters of the rate constants for addition of CH₃ at the two possible sites of the neopentyl double bond indicate that nonterminal addition is hampered by a larger energy barrier and not by an additional entropic hindrance. On the basis of the RRKM calculations, tables and expressions are provided to calculate the neopentyl radical unimolecular rate constant outside the range of conditions used in the current investigation.

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Registry No. neo-C₅H₁₁, 3744-21-6; CH₃, 2229-07-4; C₄H₈, 115-11-7.

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