ond-order linear differential equation.

(16) L. A. Pipes, "Operational Methods in Nonlinear Mechanics", Dover Publications, New York, 1965.

(17) R. Bellman, "Methods of Nonlinear Analysis VI", Academic Press, New York, 1970, p 24.

(18) First, note that the only restriction placed on $f(t)$ in the derivation of eq 1.17.11 in ref 15 is that $f(t)$ must be bounded. Thus, for differential equations of the form $u' + 2u + u^2 = f(t)$, the method of successive approximation will converge to a solution provided $f(t)$ is bounded. The substitution of $t^* = at$ followed by $x = u + 1$ reduces eq 3 to

$$u' + 2u + u^2 = \frac{b}{a} - 1 + \delta \sin(\omega t^*/a)$$

Clearly, the forcing term is bounded so that $u_n$, and hence $w_n$, will converge to solutions.

(19) Note that $x^2$ could have been calculated by differentiation of $w_2$ and substitution into eq 3 by use of eq 5. This procedure, of course, does not lead to any confusion when an exact solution is obtainable; however, in this case an expression somewhat different from eq 12 is obtained. The procedure in the main text is followed based on the somewhat arbitrary premise that the final expression for the acoustic signal should possess a $1/\omega$ dependence at low frequency.

(20) T. L. Cottrell, *Trans. Faraday Soc.*, **46**, 1025 (1950). See also ref 4 and 5 for a discussion of this effect.

(21) See, for instance, M. Abramowitz and I. Stegun, Ed., "Handbook of Mathematical Functions", National Bureau of Standards, Applied Mathematics, Series 55, 1st ed, Washington, D.C. Solve eq 16b for $R_1$ and substitute the result into eq 16a. Formula 4.6.6 is used to convert the lengthy term to $\coth^{-1}$ form. Both terms are grouped by using eq 4.6.30, the identifications following eq 17a are made, and the resulting expression simplified.

(22) H. W. Reddick and F. H. Miller, "Advanced Mathematics for Engineers", 3rd ed, Wiley, New York, 1967, p 201.

(23) See, for instance, H. B. Dwight, "Tables of Integrals and Other Mathematical Data", Macmillan, New York, 1961. The series in eq 22a can be summed by using Dwight's formula 9.04. Similarly, the expression for $b_n$ can be summed by using formula 601 and 601.1.

(24) The requirement that $\delta/b$ be small in the perturbation solution to the Riccati equation is thus equivalent to ensuring a constant mean radical lifetime throughout one cycle of irradiation.

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# Kinetic Study of the Pyrolysis of Neopentane during Its Induction Period

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Induction periods have been observed for the formation of methane and 2-methyl-1-butene in the flow pyrolysis of neopentane at 823 K. The induction periods for methane were interpreted as evidence of the approach to the steady state. Independent rate constants for the following reactions have been calculated from methane and ethane yields: $(CH_3)_4C \rightarrow CH_3 + (CH_3)_3C$, $k_1 = (1.7 \pm 0.1) \times 10^{-5}\ s^{-1}$; $CH_3 + (CH_3)_4C \rightarrow CH_4 + (CH_3)_3CCH_2\cdot$, $k_5 = (1.6 \pm 0.1) \times 10^6\ L\ mol^{-1}\ s^{-1}$; and $CH_3 + (CH_3)_2CCH_2 \rightarrow CH_4 + CH_3C(CH_2)_2\cdot$, $k_7 = 2.2 \times 10^6\ L\ mol^{-1}\ s^{-1}$. Values of the rate constant for the reaction $2CH_3 \rightarrow C_2H_6$ at 4–335 mmHg have been extrapolated to find the high-pressure limiting value, $k_{6,\infty} = (2.2 \pm 0.5) \times 10^{10}\ L\ mol^{-1}\ s^{-1}$. The induction period found for 2-methyl-1-butene indicates that this is a secondary product; the vicinal methyl radical shift reaction, $(CH_3)_3CCH_2\cdot \rightarrow (CH_3)_2\dot{C}C_2H_5$, was not observed to contribute to formation of this product.

## Introduction

The reactions of polyatomic radicals at high temperatures have proved to be difficult to investigate. Often the spectra of the radicals are unknown or too weak or insufficiently resolved from interfering spectra. Most studies have relied on interpretation of rates of product formation by using the steady-state assumption; usually, however, this assumption only permits one to determine combinations of rate constants, rather than individual rate constants.

An alternative involves the measurement of product yields during the approach to the steady state. Such studies can provide crucial information required to calculate individual rate constants.

When a reaction system is heated, there is a lag as the radical concentrations increase to their steady-state values. During this lag, or induction period, rates of product formation should be slower than the steady-state rates. Reproducible induction periods for methane formation have recently been observed during two studies[1,2] of the pyrolysis of neopentane. When the rate of the termination reaction is also measured,[1] it is possible to obtain independent rate constants for the individual radical reactions.

The objective of this article is to describe the first complete test of this method for a thermally induced reaction and to discuss the independent rate constants so obtained.

*Neopentane Pyrolysis.* The system chosen for study has again been the pyrolysis of neopentane (2,2-dimethylpropane). In the early stages of reaction, the mechanism is believed to be as follows:[1-4]

$$C_5H_{12} \rightarrow CH_3 + (CH_3)_3C\cdot \quad (1)$$

$$(CH_3)_3C\cdot \rightarrow (CH_3)_2CCH_2 + H \quad (2)$$

$$H + C_5H_{12} \rightarrow H_2 + (CH_3)_3CCH_2\cdot \quad (3)$$

$$(CH_3)_3CCH_2\cdot \rightarrow (CH_3)_2CCH_2 + CH_3 \quad (4)$$

$$CH_3 + C_5H_{12} \rightarrow CH_4 + (CH_3)_3CCH_2\cdot \quad (5)$$

$$2CH_3 \rightarrow C_2H_6 \quad (6)$$

For the present purposes, the measurements required are as follows: the rate of formation of $C_2H_6$ in the early stages, the steady-state rate of formation of $CH_4$, and the induction period for $CH_4$. From these measurements, the rate constants $k_1$, $k_5$, and $k_6$ may be calculated, as described in ref 1.

The following reactions have been proposed to account for self-inhibition and formation of minor products:[3,4]

$$CH_3 + (CH_3)_2CCH_2 \rightarrow CH_4 + CH_3C(CH_2)_2\cdot \quad (7)$$

$$CH_3C(CH_2)_2\cdot + CH_3 \rightarrow CH_2CCH_3C_2H_5 \quad (8)$$

$$2CH_3C(CH_2)_2\cdot \rightarrow (CH_3C(CH_2)_2)_2 \quad (9)$$

$$(CH_3)_3CCH_2\cdot \rightleftarrows (CH_3)_2\dot{C}C_2H_5 \rightarrow CH_2CCH_3C_2H_5 + H \quad (10)$$

$$\rightarrow (CH_3)_2CCHCH_3 + H \quad (10a)$$

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$$(CH_3)_2CCH_2 + CH_3 \rightleftarrows (CH_3)_2\dot{C}C_2H_5 \rightarrow CH_2CCH_3C_2H_5 + H \quad (11)$$

$$\rightarrow (CH_3)_2CCHCH_3 + H \quad (11a)$$

Reactions 1–6 and 10 are primary reactions, either beginning as soon as the reactant is heated or having a short induction period because of the approach to the steady-state concentrations of radicals. Reactions 7–9 and 11 are secondary reactions, occurring only after the concentration of the product, isobutene, increases. If 2-methyl-1-butene is formed by reaction 10, it should have a short induction period, like that for methane; if 2-methyl-1-butene is formed by reaction 8 or 11, it should have a much longer induction period. An induction period has not been observed in experiments down to 60 s residence time,[3] lending support to reaction 10. This reaction would involve a vicinal shift of a methyl group, a class of reaction which has not been observed, although it has been described[5] as "the most sought after" class of radical rearrangement.

*Theoretical Models.* Three models have been used to interpret the results. The first was identical with that of ref 1 and assumes that the reagent is warmed instantaneously to reaction temperature and that only reactions 1–6 occur. Methane yields were fitted by least squares to eq 12, where $a = 4(k_1k_6[C_5H_{12}])^{1/2}$ and $b = k_5[C_5H_{12}]/2k_6$.

$$[CH_4]/t = (b/t)\ln\{[1 + \exp(at)]/2\} - ab/2 \quad (12)$$

In the second model, eq 12 has been extended, as described in the Appendix,[6] to take into account the effects of reagent depletion, gas expansion, and, most importantly, self-inhibition by reactions 7 and 8. The resulting approximate equation was eq 13, where $c = 0.75ab/[C_5H_{12}]$

$$[CH_4]/t = [(b/t)\ln\{[1 + \exp(at)]/2\} - ab/2](1 - ct) - 2k_1k_7[C_5H_{12}]/a + k_7b/2 \quad (13)$$

In fitting eq 13 by least squares to experimental data, $a$ and $b$ were allowed to vary and $k_1$ was calculated from $C_2H_6$ yields. The determination of $k_7$ is described in the Results section.

In the third model, the warming of the reagent and the complete mechanism were simulated by using a computer program like that described in ref 7. The thermal diffusivity was estimated to be $(3 \times 10^{-3})[C_5H_{12}]^{-1}$ mol cm$^{-1}$ s$^{-1}$ from theoretical estimates of the thermal conductivity[8] and the heat capacity.[9] The rate constants $k_2$, $k_3$, $k_4$, and $k_8$ were obtained from ref 10–13, respectively; $k_9$ was adjusted to maintain the equality $k_8 = 2(k_{6,\infty}k_9)^{1/2}$. The remaining rate constants were adjusted to improve the fit with the experimental data.

## Experimental Section

The basic apparatus and the experimental technique was the same as used in ref 1. Five quartz reactors were used, with internal diameters and $S/V$ of, respectively, (i) 1.7 cm, 3.1 cm$^{-1}$, (ii) 0.8 cm, 9.9 cm$^{-1}$, (iii) 0.4 cm, 8.8 cm$^{-1}$, (iv) 0.3 cm, 14 cm$^{-1}$, and (v) 0.2 cm, 23 cm$^{-1}$. Along the axes of reactors i and ii were placed 0.4-cm o.d. quartz thermocouple wells. Reactors iii–v were placed along the axes of 0.8-cm i.d. quartz tubes, which held moveable platinum—platinum–13%-rhodium thermocouples. In all but two experiments, a brass tube was placed outside the reactor but inside the 45-cm long furnace to improve thermal contact. Computer analysis of typical temperature profiles indicated that 88% of the reaction occurred within ±2 K of the average reaction temperature.

The gas chromatograph was calibrated each day with a mixture of $N_2$ with hydrocarbons whose concentrations were similar to those in the reaction products. 2-Methyl-1-butene was separated at 0 °C on a 1-m, 10% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb W column in series with a 3-m, 10% DC-200 silicone oil on Chromosorb W column.

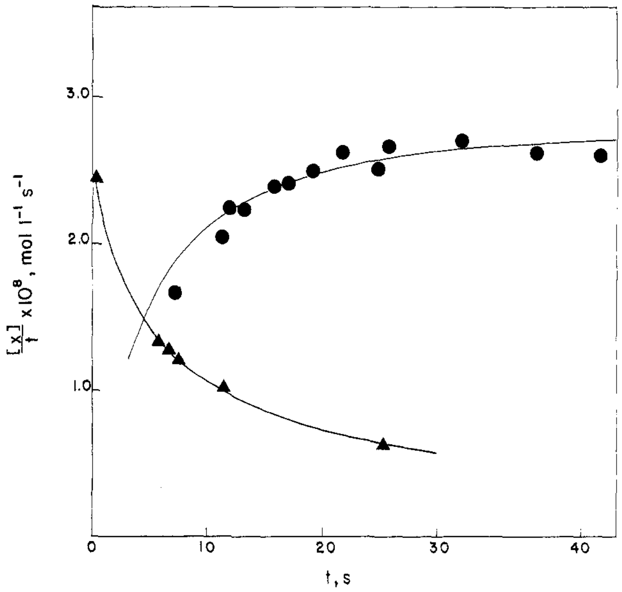

**Figure 1.** Dependence of the rate of formation of X on the reactor residence time at 73 torr and 823 K: (●) X = 2-methyl-1-butene; (▲) X = ethane.

The major impurity in neopentane was isobutane. The $C_2H_6$ impurity was 1 ppm. $CH_4$ impurity was not detected.

## Results

Experiments have been performed to observe the establishment of the steady state at reactor temperatures of 822 ± 1 K, at reactant pressures of 4–28 torr, and at reactor residence times from 0.04 to 1.5 s. In ancillary experiments, pressures have extended to 335 torr and residence times to 100 s.

Minor products observed were ethylene, propylene, propane, 2-methyl-1-butene, and 2-methyl-2-butene. 2,2-Dimethylbutane was not observed, indicating that its rate of formation was less than 1% of that of ethane.

The yield of $C_2H_4$ was 7–13% of that of $C_2H_6$ in experiments from 28 to 96 torr. The order of formation of $C_2H_4$ was 1.48 ± 0.11, compared to 1.43 ± 0.04 for $CH_4$ and 1.04 ± 0.02 for $C_2H_6$. (Unless otherwise specified, quoted uncertainties are standard deviations).

As shown in Figure 1, an induction period has been found for 2-methyl-1-butene in experiments at 823 K and 73 torr. In the simulation, shown as the smooth curves, values of $k_5$ ($1.6 \times 10^6$ L mol$^{-1}$ s$^{-1}$) and $k_6$ ($1.6 \times 10^{10}$ L mol$^{-1}$ s$^{-1}$) were selected to agree with experiments described later, in which induction periods were observed for $CH_4$. To provide agreement with the data in the figure, the remaining rate constants were chosen as $k_1 = 1.8 \times 10^{-5}$ s$^{-1}$, $k_7 = 2.2 \times 10^6$ L mol$^{-1}$ s$^{-1}$, $k_{10} = 0$, $k_{11} = 1.2 \times 10^6$ L mol$^{-1}$ s$^{-1}$. The yields of 2-methyl-2-butene were one-fifth of those of 2-methyl-1-butene.

Figure 2 shows data for $CH_4$ from experiments at 822 K and 28 torr. The dashed and solid curves are least-squares fits to the data using, respectively, eq 12, without self-inhibition, and eq 13, with the self-inhibition rate constant, $k_7$, found in fitting the data in Figure 1. Including self-inhibition decreased the calculated value of $k_5$ by 2% and the value of $k_6$ by 8%. The dotted curve shows the results of a computer simulation using the same rate constants as those found with the smooth curve. The slight difference in these curves is the result of inclusion of extra reactions and the thermal diffusivity in the simulation. The agreement could be improved if $k_1$ in the

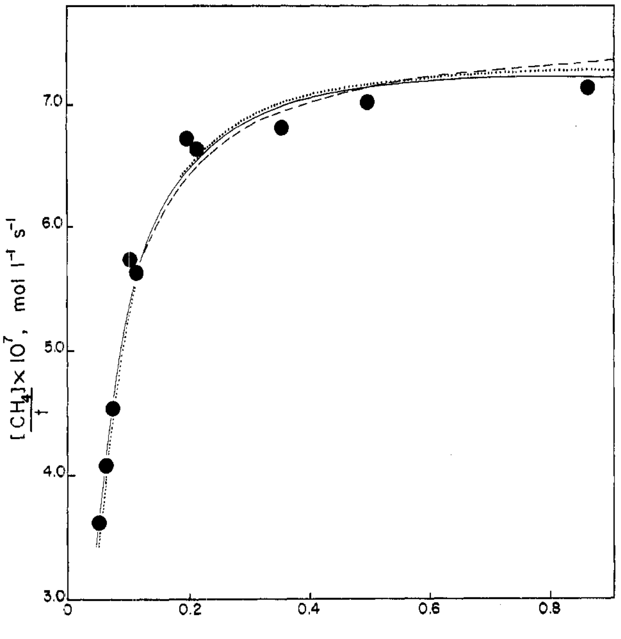

**Figure 2.** Dependence of the rate of formation of methane on the reactor residence time at 28 torr and 822 K: (- - -) least-squares fit to eq 12; (—) least-squares fit to eq 13; (· · ·) computer simulation.

TABLE I: Rate Constants Determined

| $P$, mmHg | reactor diam, mm | $10^5 k_1$, s$^{-1}$ | $10^{-6} k_5$, L mol$^{-1}$ s$^{-1}$ | $10^{-10} k_6$, L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 4.2 | 4 | 1.77 | 1.72 | 0.66 |
| 7.6 | 8 | 1.60 | 1.57 | 0.81 |
| 7.6 | 8[a] | 1.62 | 1.62 | 0.88 |
| 11.2 | 4 | 1.54 | 1.45 | 0.95 |
| 17.3 | 2 | 1.83 | 1.80 | 1.14 |
| 17.6 | 3 | 1.82 | 1.64 | 1.01 |
| 17.3 | 4 | 1.70 | 1.46 | 1.06 |
| 28.0 | 3 | 1.71 | 1.76 | 1.39 |
| 46.0 | 3 | 1.76 | | 1.56 |
| 71.0 | 2 | 1.79 | | 1.58 |
| 96.0 | 4 | 1.93 | | 1.75 |
| 335.0 | 2 | 1.64 | | 1.85 |
| av | | 1.73 ± 0.11 | 1.63 ± 0.12 | |

[a] KCl coated reactor.

simulation were increased by 2%, $k_5$ by 3%, and $k_6$ by 6%. The resulting values are listed in Table I.

At lower pressures the simulations were in even closer agreement to the fits of eq 13, and the latter method was used to determine the rate constants quoted in Table I.

At higher pressures, the induction periods predicted by the simulation were more strongly affected by the delay in warming the reagent. The listed values of $k_6$ were calculated from the experimental values of $k_1$, the measured rate of $CH_4$ formation (yielding $k_1^{1/2}k_5k_6^{-1/2}$) and from the average value of $k_5$ in Table I.

The table also shows the results of experiments with different surfaces. The third line shows the results of experiments with a reactor coated with KCl, instead of the usual quartz surface. Also shown are the results of experiments at similar pressures (17.3–17.6 torr) but differing reactor diameter and surface-to-volume ratio.

It can be seen from Table I that the values of $k_1$ and $k_5$ were found to be independent of pressure, within a standard deviation of 7%. The values of $k_6$ increased with an increase in pressure, as shown graphically in Figure 3. The solid and dashed curves, respectively, were calculated from the RRKM model of Clark and Quinn[14] and from a Kassel curve[15] with $S = 5$ and $B_k = 20$.

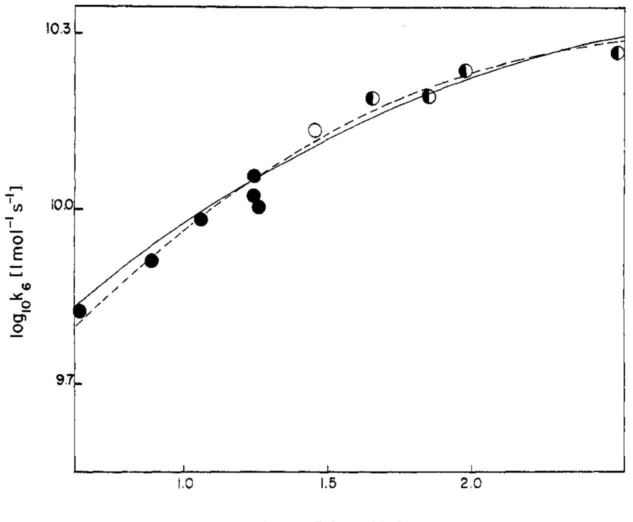

**Figure 3.** Logarithmic pressure dependence of $k_6$: (●) from least-squares fits to eq 13; (○) from computer simulations; (◐) from experimental measurements of $CH_4$ and $C_2H_6$ formation and from the average value of $k_5$ in Table I. (—) RRKM model of Clark and Quinn;[14] (- - -) Kassel curve.[15] Both curves were adjusted vertically and horizontally to improve the fit.

Both curves were adjusted vertically and horizontally to minimize the sum of the squares of their differences from the data points. The resulting collisional deactivation probabilities, $\beta$, were found to be 0.4 and 0.2 for the two curves, respectively. The high-pressure limiting rate constants, $k_{6,\infty}$, were found to be $(2.3 \pm 0.2) \times 10^{10}$ L mol$^{-1}$ s$^{-1}$ and $(2.1 \pm 0.1) \times 10^{10}$ L mol$^{-1}$ s$^{-1}$, respectively. Use of larger values of $S$ in the Kassel model led to intermediate values of $k_{6,\infty}$.

## Discussion

*Possible Systematic Errors.* The calculation of $k_1$ has assumed that reaction 6 is the only termination reaction and the only source of $C_2H_6$. According to the simulations, the most important competing terminations would be reaction 8 and the recombination of $CH_3$ and $(CH_3)_3CCH_2\cdot$. However, $(CH_3)_3CCH_2CH_3$ was not observed as a product, so the rate of the latter reaction must be 1% or less of the rate of reaction 6. From the calculations for Figure 1, it is found that the rate of reaction 8 is only 0.3% of the rate of reaction 6 during the establishment of the steady state. Furthermore, because of the similarity in their reaction orders, $C_2H_4$ must have been formed by a process parallel to the formation of $CH_4$, that is, by a minor propagating step, such as the attack of methyl radicals on an impurity, as suggested in ref 4, and not by a termination process. We conclude that reaction 6 is the only significant termination process.

Some of the $C_2H_4$ may result from the decomposition of $C_2H_5$ radicals formed from an impurity; $C_2H_5$ could also form $C_2H_6$ by abstraction. In a similar system,[16] $C_2H_5$ radicals were found to yield $C_2H_4$ three times more frequently than $C_2H_6$. In the present system, it can be estimated that 4% or less of the $C_2H_6$ comes from this source.

Possible competing sources of $CH_4$ have been shown to contribute a maximum of 0.5% in ref 17.

Table I and Figure 3 do not show any significant effect of the surface on the rate constants determined.

Possible competitors to the secondary reactions (reactions 7–9 and 11) are more difficult to eliminate, as less is known about these reactions and the present data are

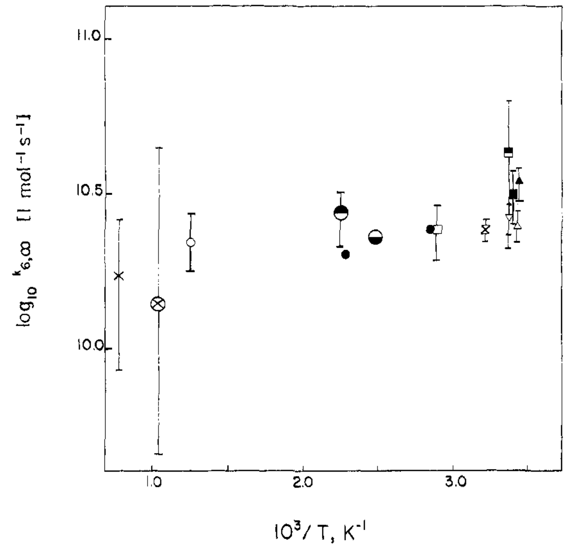

**Figure 4.** Arrhenius plot for $k_{6,\infty}$: (⊗) ref 7; (◒) ref 15; (●) ref 20; (⊖) ref 21; (△) ref 22; (▽) ref 23; (⊠) ref 24; (□) ref 25; (▲) ref 26; (■) ref 27; (X) ref 28; (⊟) ref 29; (O) this work.

less extensive. Possible decomposition or abstraction reactions of methylallyl radicals have not been observed in previous studies of neopentane pyrolysis.[3,4] If they do occur, the reported value of $k_7$ should be increased, but there would be little change in the values of $k_1$, $k_5$, and $k_6$. Other association–dissociation processes could contribute to the formation of the methylbutenes; in this case the reported values of $k_{11}$ and $k_{11a}$ should be decreased.

*Comparison with Other Work.* Because of improvements in calibration, the rate constants quoted herein are believed to be more reliable than those in ref 1 and 17.

The average value of $k_1 \times 10^5$ (s$^{-1}$), 1.7, in Table I is within the range of values calculated from Arrhenius parameters determined in other laboratories: 0.9,[3] 1.7,[4] 1.2,[18] and 1.9.[19]

There are no other independent measurements of $k_5$, but the value of $k_5k_{6,\infty}^{-1/2}$, 11 L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$, calculated from this work is in good agreement with the value, 12 L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$, calculated from Arrhenius parameters[4] determined at 713–823 K. This supports the earlier conclusion[17] that the Arrhenius plot for this reaction is a curve.

The product, $k_1k_{6,\infty}$, determined from the induction periods, was found to be $3.8 \times 10^5$ L mol$^{-1}$ s$^{-2}$, in excellent agreement with a value, $4.5 \times 10^5$ L mol$^{-1}$ s$^{-2}$, predicted from Arrhenius parameters calculated from induction periods found at 703–743 K.[2]

Combining uncertainities in the data, in the treatment of the data and in the extrapolations in Figure 3, we estimate $k_{6,\infty}$ to be $(2.2 \pm 0.5) \times 10^{10}$ L mol$^{-1}$ s$^{-1}$. Determinations of $k_{6,\infty}$ at various temperatures are compared in Figure 4. It appears that $k_{6,\infty}$ remains constant or decreases slightly as temperature increases. This contradicts a common form of RRKM theory, which predicts a substantial increase with increasing temperature.[7,28]

A value of $k_{6,\infty}$ at 838 K of $2.0 \times 10^{10}$ L mol$^{-1}$ s$^{-1}$ has been estimated from the rate constant for the reverse reaction and thermochemistry.[30] The excellent agreement with the present work provides confirmation for the thermochemistry of this reaction[31] ($\Delta H^\circ_0 = -87.76$ kcal mol$^{-1}$).

The value of the rate constant, $k_7$, determined in simulating the data in Figure 1, $2.2 \times 10^6$ L mol$^{-1}$ s$^{-1}$, is the first independent measurement. The quotient $k_7k_{6,\infty}^{-1/2}$ can be compared with earlier determinations, as shown in Figure 5. The other high-temperature points were determined by simulating previous neopentane pyrolysis experiments. The straight line is a least-squares fit to the low-temperature, photolysis data. The pyrolysis data lie above this line, suggesting a small amount of curvature of the Arrhenius plot. The degree of curvature would be increased if additional reactions of the methylallyl radical occur.

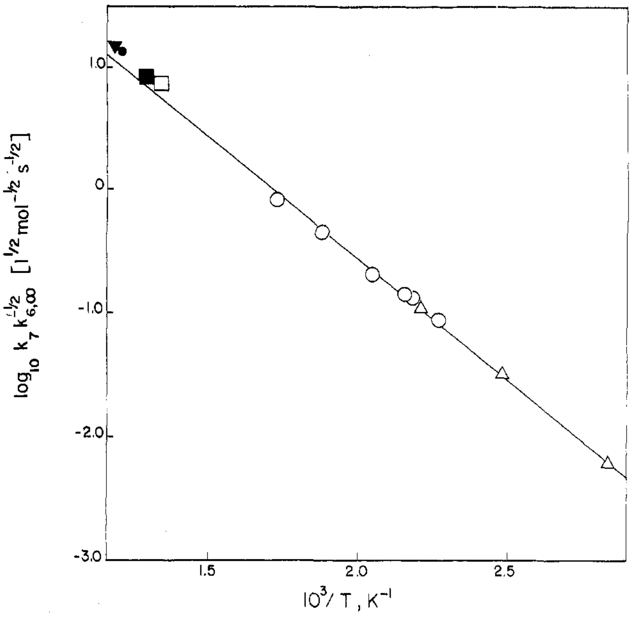

**Figure 5.** Arrhenius plot for $k_7k_{6,\infty}^{-1/2}$: (■, □, ▼) from computer simulations of ref 3, 4, and 17, respectively; (△) ref 32; (O) ref 33; (●) this work.

The induction period found for 2-methyl-1-butene indicates that the vicinal methyl radical shift rearrangement, reaction 10, is not a significant source of this product. The radical–olefin association–dissociation rate constants, $k_{11} = 1.2 \times 10^6$ L mol$^{-1}$ s$^{-1}$ and $k_{11a} = 0.5 \times 10^6$ L mol$^{-1}$ s$^{-1}$, may be compared with estimates of $0.2 \times 10^6$ L mol$^{-1}$ s$^{-1}$ for both reactions, based on the overall thermochemistry[9,31] and the rate constants[34] for addition of H to isobutene and to *trans*-butene, assumed similar to 2-methyl-1-butene and methyl-2-butene, respectively.

## Conclusion

Product analysis under conditions for which the steady-state assumption is not valid has been shown to provide a useful method of determining independent rate constants for radical reactions. Its use requires that the mechanism be reasonably simple and well understood and that experimental conditions be carefully chosen. If the reaction pressure or temperature were reduced, $C_2H_6$ yields would decrease, making it impossible to determine the required initiation rate constant. If the reaction temperature or pressure were increased, induction periods would become too short to measure in a flow system. Because of the limited accessible temperature range, it would be difficult to determine precise Arrhenius parameters by this technique.

Although it cannot provide precise activation energies on its own, this technique in combination with others can contribute to knowledge of activation energies. For example, the data from the literature in Figure 6 are consistent with an activation energy from −3 to 0 kJ mol$^{-1}$ for reaction 6. The results of this work have reduced this uncertainty to about one-half. This is important, as Arrhenius parameters for over 100 reactions[17,32-34] have been determined relative to $k_6$.

In Figure 2, values of $k_1$, $k_5$, and $k_6$ were found to be little affected by changes in other parameters of the model. Values of $k_5$ were internally consistent within a standard deviation of 7% over a sevenfold experimental range of

J. Phys. Chem. **1980**, *84*, 2225-2233

pressure. This adds confidence to the establshed mechanism. It was shown that 2-methyl-1-butene is predominantly a secondary product, formed by reaction 8 and another source, probably reaction 11. The rate constants $k_5$ and $k_7$ have been measured individually, a task which has not been possible by earlier techniques.

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*Supplementary Material Available:* An Appendix describing the derivation of eq 13 (2 pages). Ordering information is given on any current masthead page.

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# Energy Transfer Reactions of $N_2(A^3\Sigma_u^+)$. 5. Quenching by Hydrogen Halides, Methyl Halides, and Other Molecules

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The 300 K quenching rate constants for $N_2(A^3\Sigma_u^+, v'=0,1)$ have been measured with 20 small molecules, mostly of the hydrogen halide or methyl halide variety. The metastable $N_2(A)$ molecules were prepared by the reaction of $Ar(^3P_{0,2})$ with $N_2$ in a discharge-flow system. Rate constants were measured by observing the variation of the $N_2(A^3\Sigma_u^+ - X^1\Sigma_g^+)$ emission intensity as a function of added reagent concentration. The magnitude of the rate constants increase in both the HX and $CH_3X$ series as X changes from F to I. The temperature dependence of the NO, $O_2$, $C_2H_2$, and $C_2H_4$ reactions were qualitatively investigated with the discharge flow technique by doing experiments at ~120 K. On the basis of the limited data, the rate constants are either virtually invariant with temperature or decrease mildly with decreasing temperature. In contrast the $N_2(A)$ bimolecular, energy pooling, $N_2(C)$ formation rate constant appears to increase with decreasing temperature. The results of the present study are compared to previous investigations from this laboratory and to other studies of $N_2(A^3\Sigma_u^+)$.

## Introduction

During recent years, several methods have been developed which faciliate direct study of the chemistry of $N_2(A^3\Sigma_u^+)$, the first electronically excited state of molecular nitrogen, in the absence of other reactive intermediates.[1-6] The method developed in our laboratory utilizes a discharge-flow apparatus in which the reaction of $Ar(^3P_{0,2})$ with $N_2$ is used to convert the metastable argon atoms into metastable $N_2(A^3\Sigma_u^+)$ molecules, via cascade from higher lying triplet states of $N_2$.[7] This method provides a continuous flow of $N_2(A)$ molecules, in the $v' = 0$ and 1 levels, at a concentration of $\sim 2 \times 10^{10}$ molecules cm$^{-3}$. A new use[8] of this $N_2(A)$ source is the investigation of the chemistry of $N_2(B^3\Pi_g)$, which can be produced by laser excitation from $N_2(A)$. A similar discharge flow source has been developed for the study of $CO(a^3\Pi)$.[9] Since the $N_2(A)$ discharge-flow source gives a mixture of $v' = 0$ and 1 levels (1.0:0.77 for the operating conditions of the present study), the rate constant measurements must be evaluated carefully to determine the role, if any, of vibrational excitation. Using pulse radiolysis, Dreyer and co-workers[5] have studied the kinetics of $N_2(A)$ in even higher vibrational levels. In our earlier work we studied the quenching reactions of $N_2(A)$ with some common inorganic and unsaturated organic molecules,[1b,c] observed excitation transfer for some reactions,[1c-e] and compared the reactivity of

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