culated by using the normal values for bond lengths and bond angles in alkynes.[36] The symmetry number for external rotation is 2, and the group additivity value for $S°_{300}$ was assumed correct.

The frequencies of the six-membered ring transition state were chosen according to the Benson–O'Neal procedure[17,25] and adjusted to yield the selected $A$ factors. The moments of inertia were calculated for transition-state geometries corresponding to typical "aromatic" structures.[37] In the case of HDE, three hindered internal rotations, together with some of the low-frequency bending modes (mainly skeletal), were replaced by higher-frequency, out-of-plane, ring-bending modes. The hindered internal rotation about $C_3$–$C_4$ was taken as the reaction coordinate, and the torsion about $C_1{=}C_2$ was replaced by a three-electron torsion. There are some minor contributions from changes in stretching modes. For HDY a similar procedure was adopted except that only two rather than three hindered internal rotations are lost in forming the transition state and there is no torsion about the carbon–carbon triple bond.

The parameters for the RRKM calculations are summarized in Tables I and II.

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# Multiphoton Infrared Laser-Induced Decomposition of Acetone-$d_6$[1]

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The focused IR laser-induced decomposition of acetone-$d_6$ has been studied to determine if the classical mechanism for the thermal decomposition can explain the distribution of reaction products. Binary mixtures of acetone-$d_6$ with acetone, ethane, $(CH_3)_2N_2$, and cyclopropane have been studied for product composition and isotopic distribution in the products. It is argued on the basis of these observations that ketene is not produced and a classical acetone chain mechanism cannot explain the facts. The material balance and the production of hydrogen and ethylene as major products are best explained on the basis of total decomposition of acetone-$d_6$ near the focus. This is followed by a rapid temperature rise resulting from recombination of $CD_3$. The chemistry that follows is simply the thermal decomposition of ethane at temperatures approaching 1900 K.

## Introduction

The early experimental results in the multiphoton infrared (focused) decomposition of acetone-$d_6$ have been found to be consistent with a mechanism involving a purely thermal reaction in which the laser serves to raise the temperature to about 1250 K within 0.1 μs.[2] Acetone-$d_6$ then decomposes much more slowly into two methyl radicals and CO. Concurrent reactions of the methyl radicals produce methane and ethane (reactions 1–3). It was

$$CD_3COCD_3 \rightarrow 2CD_3 + CO \tag{1}$$

$$CD_3 + CD_3COCD_3 \rightarrow CD_4 + COCD_2 + CD_3 \tag{2}$$

$$2CD_3 + M \rightarrow C_2D_6 + M \tag{3}$$

shown that the ratios of the rates of formation of methane and ethane are quantitatively consistent with the concept

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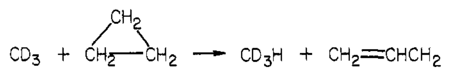
TABLE I: Hydrocarbon Reaction Products (Mol %) in Multiphoton Decomposition of Acetone-$d_6$

| $T$, °C | $P(CD_3COCD_3)$, torr | no. of pulses | methane | ethane | ethylene | acetylene | propane |
|---|---|---|---|---|---|---|---|
| 25 | 20 | 10 | 28.3 | 34.2 | 27.7 | 7.7 | 2.1 |
| 25 | 20 | 10 | 28.9 | 32.2 | 28.2 | 7.9 | 2.1 |
| 25 | 20 | 80 | 30.3 | 35.7 | 25.0 | 7.0 | 2.0 |
| 78[a] | 20 | 1 | 33.2 | 29.8 | 27.3 | 7.6 | 2.1 |
| 25[a] | 20 | 1 | 33.4 | 29.3 | 27.5 | 7.7 | 2.1 |
| 25 | 5 | 10 | 8.9 | 67.7 | 12.0 | 0.1 | 2.4 |

[a] 2-cm$^3$ reaction cell, 10-cm focal length lens.

of thermal equilibrium and the known kinetics of reactions 1–3, assuming the stationary state in methyl radicals is maintained. However, such an interpretation is not unique and it is possible that the stationary state hypothesis accounts for the facts on a purely circumstantial basis. The present work was undertaken to extend the early experiments to include exhaustive product analysis, material balance, and isotopic scrambling in an effort to assess the relative merits of the classical free-radical mechanism and of alternatives that might rationalize the results as well or better.

Among the consequences of the mechanism involving reactions 1–3 are that for long chains (a) $CD_4 \gg C_2D_6$, (b) $CD_4 \gg CO$, and (c) $CD_2CO \sim CD_4$. Further, acetone-$d_6$ being by far the most abundant hydrogen donor in the system should be the only molecule attacked by methyl radicals. Finally, if the decomposition of acetone-$d_6$ is carried out in the presence of other hydrogen donors the rate of abstraction of D in reaction 2 should be consistent with the known rates of abstraction of H from the hydrogen donors such as those indicated in reactions 4–6.



$$CD_3 + (CH_2)_3 \rightarrow CD_3H + CH_2{=}CHCH_2 \qquad (4)$$

$$CD_3 + C_2H_6 \rightarrow CD_3H + C_2H_5 \qquad (5)$$

$$CD_3 + CH_3COCH_3 \rightarrow CD_3H + CH_2COCH_3 \qquad (6)$$

## Experimental Section

All experiments were done by using a pulsed (0.6 Hz) $CO_2$ TEA laser. The energy of the beam was about 0.8 J per pulse at 9.68 μm. A Pyrex reaction cell, which carried sodium chloride windows at front and rear, was used. The cell was 2.5 cm in diameter and 7 cm in length. A sodium chloride lens of 5-cm focal length was employed. Two mildly focusing mirrors reduced the beam diameter below that of the lens in front of the cell window. The focus was at the center of the cell. After exposure to the laser beam, about one quarter of the contents of the cell was directed to a gas chromatograph by an appropriate valving system. Sufficient reaction products for chromatographic analysis were readily obtained with a single laser pulse. The column used was Poropak Q (1 m, $^1/_4$-in. copper tubing) and the detector employed flame ionization. A few experiments were done by using a Porasil C chromatographic column to search for acetylene. Some reactions were carried out by using ten or more laser pulses. In some experiments a Pyrex reaction cell of dimensions similar to that described, but with provision for cooling to 77 K or other low temperature, was used for mass spectral analyses of CO, methane, and hydrogen. The P34 line of the $CO_2$ TEA laser spectrum used as the exciting frequency corresponds to the $B_1$ vibration of the out-of-phase combination of the in-plane asymmetric deformation of acetone-$d_6$.[3] Standard samples of $CD_4$, $CD_3H$, $CD_2H_2$, $CH_3D$ (Merck), $CH_4$, $CO_2$, $D_2$, and $H_2$ were used to calibrate the mass spectrometer. Pure samples of hydrocarbons were used to calibrate the gas chromatograph.

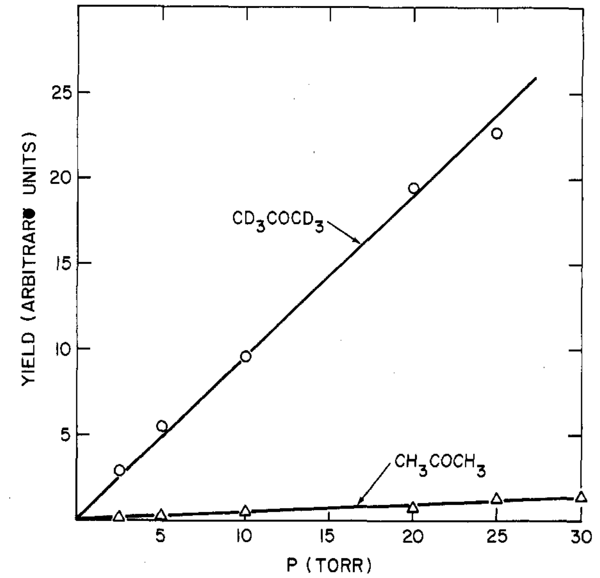


Figure 1. Total product yield per pulse in the decomposition of neat acetone and acetone-$d_6$.

## Results

1. *Decomposition of Neat Acetone and Acetone-$d_6$.* The P34 line of the TEA laser (9.68 μm) is much more effective in decomposing acetone-$d_6$ than acetone as shown in Figure 1. In each case the amount of reaction is closely proportional to the pressure. Acetone-$d_6$ decomposes by a factor of 21 more extensively than acetone.

2. *Reaction Products and Material Balance.* In the early stages of the present work[2] ethylene and acetylene were not detected since the alumina chromatographic column used is not suited to their measurement and their presence was not suspected. Subsequently, a 1 m long, $^1/_4$-in. diameter Poropak Q column was used and ethylene was found to be a major reaction product. In other experiments, a Poracil C column was used to reveal the presence of acetylene among the products. Mass spectrometric analysis showed hydrogen to be an important reaction product. Table I presents the composition of the hydrocarbon products and shows that the product distribution is insensitive to ambient temperature between 25 and 78 °C and to the number of pulses employed. It is noteworthy that acetylene production is very sensitive to acetone-$d_6$ pressure, while propane is quite insensitive as shown in Figure 2. Traces of propylene and $n$-butane were found but are not reported in Table I.

The ratio of ethylene to methane in the products is remarkably insensitive to pressure. However, the ethane/methane ratio is very pressure sensitive as previously noted.[2] Figure 3 shows the ethane/methane ratio as a function of pressure of acetone-$d_6$ from 2.5 to 80 torr. The solid line is calculated from the stationary state mechanism.[2] The experimental ratios fall well above this line at pressures below 7 torr and below the line at higher pressures. At lower acetone-$d_6$ pressures, the methane

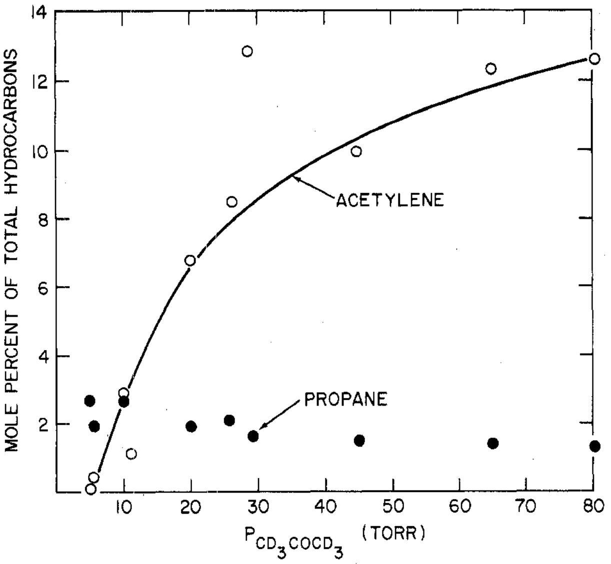


Figure 2. Effect of pressure on propane and acetylene yield in the decomposition of acetone-$d_6$.

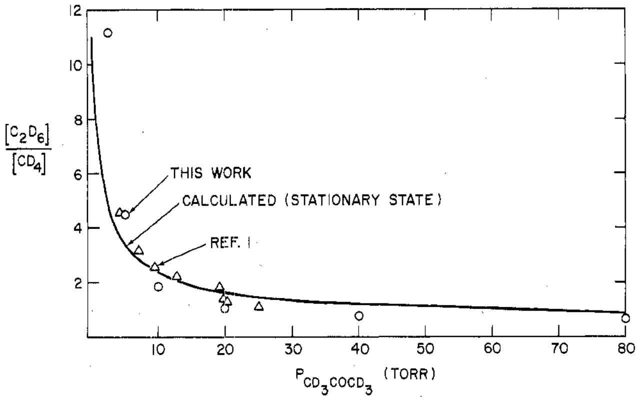


Figure 3. Effect of pressure on product ratio $[C_2D_6]/[CD_4]$ in the decomposition of acetone-$d_6$.

TABLE II: Material Balance in $CD_3COCD_3$ Decomposition

| constituent | mol % | constituent | mol % |
|---|---|---|---|
| CO | 40.9 | $C_2D_4$ | 11.8 |
| $D_2$ | 11.7 | $C_2D_6$ | 17.0 |
| $CD_4$ | 14.4 | $C_3D_8$ | 0.8 |
| $C_2D_2$ | 3.4 | | |

Empirical Formula $C_{3.0}D_{6.1}O_{1.0}$

TABLE III: Rate Constants for Abstraction by $CD_3$ Radicals

| reaction | rate constant, $mol^{-1}\ cm^3\ s^{-1}$ |
|---|---|
| 2 | $3.55 \times 10^{10}T^{1/2}\ \exp(-11300/RT)$ |
| 4 | $4.62 \times 10^{10}T^{1/2}\ \exp(-13100/RT)$ |
| 5 | $4.3 \times 10^{10}T^{1/2}\ \exp(-11500/RT)$ |
| 6 | $2.73 \times 10^{10}T^{1/2}\ \exp(-9630/RT)$ |
| 7 | $4.3 \times 10^{10}T^{1/2}\ \exp(-12970/RT)$ |

TABLE IV: $[CD_3H]/[CD_4]$ Product Ratios, Experimental and Calculated, in Decomposition of Mixtures of $(CD_3)_2CO$ and RH

| | | | | $[CD_3H]/[CD_4]_{calcd}$[a] | |
|---|---|---|---|---|---|
| RH | $P_{RH}$, torr | $P_{(CD_3)_2CO}$, torr | $[CD_3H]/[CD_4]_{expt}$ | 1250 K | 2000 K |
| c-$C_3H_6$ | 5.0 | 20.0 | 0.40 | 0.16 | 0.21 |
| $C_2H_6$ | 10.0 | 10.0 | 1.08 | 1.12 | 1.15 |
| $(CH_3)_2CO$ | 10.0 | 10.0 | 1.50 | 1.50 | 1.17 |

[a] Calculated from eq 8 and its analogues.

product falls off so drastically that the methane/ethane ratios are difficult to measure accurately. Thus, the 5-torr run reported in Table I in which a Poropak Q column was used for analysis is not in good agreement with those data[2] in Figure 1 obtained by using an alumina column for analysis. A mass spectrometric search was made for ketene by examining the fraction of the reaction mixture volatile at the temperature of melting ethyl bromide (154 K) after having pumped off hydrogen, carbon monoxide, and methane at 77 K. No ketene was found, although a small amount may have escaped detection. The photolysis of a mixture of 10 torr acetone + 10 torr acetone-$d_6$ (700 pulses) showed that the dominant products (other than those volatile at 77 K) volatile at 154 K are ethane and ethylene. A rough isotopic analysis showed the ethane composition to be $C_2D_6$:$CH_3CD_3$:$C_2H_6$ approximately 1:2:1. However, it is evident that $C_2D_5H/C_2D_6$ is about 0.3 and some isotopic scrambling has taken place. Further, the ethylene fraction contains an amount of $C_2D_3H$ comparable to that of $C_2D_4$. A more detailed isotopic description of ethane and ethylene was not possible. According to the mechanism suggested in ref 1, an amount of ketene equivalent to the methane should have been produced if the chains are long. It is difficult to imagine this much ketene escaping detection. A measure of material balance was obtained from the composition of the products of acetone-$d_6$ photolysis obtained from a two-part analysis of the products of one reaction. The first partial analysis was of products volatile at 77 K ($D_2$, CO, $CD_4$). The second was a chromatographic analysis for hydrocarbons. The overall product analysis was determined by linking the two partial analyses by means of the common constituent, methane. The results of one such dual analysis are presented in Table II. One other such experiment gave excellent corroboration of the empirical formula. The excellent material balance suggests strongly that no large amounts of ketene are produced, since an amount of ketene equal to methane (as the long-chain, stationary state thermal mechanism demands) would have produced an empirical formula $C_{2.7}D_{5.1}O_{1.0}$, a result far from the empirical formula for acetone-$d_6$, $C_3D_6O$. The empirical formula derived from the product analysis is probably accurate to 0.1 atom of carbon and hydrogen, so that the observed empirical formula, $C_{3.0}D_{6.1}O_{1.0}$, is within experimental error identical with that of acetone-$d_6$.

*3. Decomposition of Acetone-$d_6$ in the Presence of Hydrogen Donors.* In an effort to measure a "diagnostic temperature" in the reaction zone, the presumed D donor, acetone-$d_6$, was made to compete with H donors for $CD_3$. Rate constants and activation energies for reactions of $CD_3$ with cyclopropane,[4] ethane,[5] and acetone[6] have been measured directly relative to those for reaction of $CD_3$ with acetone-$d_6$ at temperatures from 500 to 800 K. Extrapolation of $[CD_3H]/[CD_4]$ product ratios to higher temperatures involves an error estimated to be ±20%[5] at 2000 K.

Table III presents the rate constants used in the extrapolations plus that for an additional reaction (reaction 7). Table IV compares experimental ratios of $[CD_3H]/[CD_4]$ with those calculated from eq 8 and its analogues for 1250 K, the "diagnostic temperature" previously deduced,[2] and for 2000 K, the temperature we now believe to be more realistic.

$$CD_3 + C_2D_6 \rightarrow CD_4 + C_2D_5 \qquad (7)$$

$$[CD_3H]/[CD_4] = \frac{k_4[\text{c-}C_3H_6]}{k_2[(CD_3)_2CO]} \qquad (8)$$

TABLE V: Decomposition of Mixture of $(CH_3)_2N_2$ + $(CD_3)_2CO$ (12 torr Each)

| | $[CD_3H]/[CD_4]_{calcd}$ | |
|---|---|---|
| $[CD_3H]/[CD_4]_{expt}$ | 1250 K | 2000 K |
| 1.49 | 0.36 | 0.21 |

TABLE VI: Hydrocarbon Product Analysis for Reaction of 9 torr of $(CH_3)_2N_2$ + 12 torr of $(CD_3)_2CO$

| product | mol % | product | mol % |
|---|---|---|---|
| hydrogen | 12 | ethylene + acetylene[a] | 9 |
| methane | 16 | ethane | 63 |

[a] Ethylene and acetylene are not resolved on the Poropak Q column used.

TABLE VII: Methane and Hydrogen Analysis in Decomposition of a Mixture of 10 torr of $CD_3COCD_3$ + 10 torr of $CH_3COCH_3$

| | methane | | | | | hydrogen | | |
|---|---|---|---|---|---|---|---|---|
| species | $CD_4$ | $CD_3H$ | $CH_2D_2$ | $CH_3D$ | $CH_4$ | $D_2$ | HD | $H_2$ |
| mol % | 20.7 | 31.6 | 15.5 | 19.5 | 12.5 | 23.3 | 49.7 | 27.0 |

It is estimated[5] that the error in the calculated ratio $[CD_3H]/[CD_4]$ at 2000 K is ±20% (standard deviation). Scrambling reactions, e.g., reaction 9, tend to elevate the

$$CD_3 + H \rightarrow CD_2H + D \qquad (9)$$

experimental ratios, $[CD_3H]/[CD_4]$, by as much as 25%. The data in Table IV are, therefore, consistent with a mechanism involving attack by $CD_3$ on the parent acetone-$d_6$ (reaction 2) at 2000 K except that the experimental ratio with cyclopropane seems too high. It is possible, however, that the unimolecular conversion of cyclopropane to propylene occurs so rapidly that $CD_3H$ is formed mainly by abstraction from the more labile hydrogen atoms of propylene.

Table V compares the experimental $[CD_3H]/[CD_4]$ ratio from decomposition of a mixture of $(CH_3)_2N_2$ and $(CD_3)_2CO$ with the ratio calculated on the assumption that reaction 2 is the source of $CD_4$ and reaction 10 is respon-

$$CD_3 + (CH_3)_2N_2 \rightarrow CD_3H + CH_2N_2CH_3 \qquad (10)$$

sible for production of $CD_3H$.[7] Although the kinetic ratio of the competition between reactions 2 and 10 was not measured[7] directly, the absolute rate constant for reactions 2 and 10 gives a calculated $[CD_3H]/[CD_4]$ (Table V) which is difficult to reconcile with a mechanism involving reaction 2 as the source of $CD_4$.

The information presented in Table VI shows that ethane production is greatly enhanced relative to other hydrocarbon products when $(CD_3)_2CO$ is decomposed in the presence of $(CH_3)_2N_2$. Neat $(CH_3)_2N_2$ shows no measureable decomposition when exposed to the 9.68-μm laser radiation.

4. *Isotopic Distribution in Methane and Hydrogen Fractions. a. Acetone + Acetone-$d_6$ Mixtures.* Earlier,[2] it was reported that the decomposition of mixtures of $CD_3COCD_3$ and $CH_3COCH_3$ gave approximately equal amounts of methanes derived from $CD_3$ and $CH_3$. Any $CH_2D_2$ present was obscured by the $H_2O$ background and somewhat uncertain $CD_3H$ and $CD_4$ cracking patterns. A much more detailed analysis of the methane isotopes was carried out in the present work. Table VII shows a typical methane/hydrogen analysis obtained from the products volatile at 77 K. Several duplicate analyses confirmed that $CH_2D_2$ was present in substantial amounts. Secondly, the $[CD_3H]/[CD_4]$ ratio was considerably larger than $[CH_4]/[CH_3D]$, a result not compatible with the known isotope effects. A third characteristic of the methane analysis is that there is a deuterium bias in the methane, i.e., the ratio $[D]/[H] > 1$. No bias exists in the hydrogen fraction and the ratio $[HD]^2/([H_2][D_2]) = 3.9$, is a value close to that expected from an atomic mechanism.

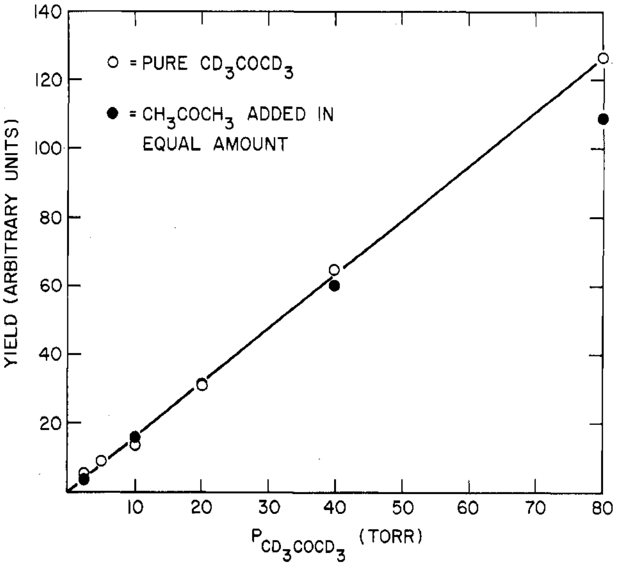


**Figure 4.** Effect on total yield per pulse of addition of acetone to acetone-$d_6$.

*b. Acetone-$d_6$ + Ethane Mixture.* Table VIII gives isotopic analyses for the methane and hydrogen products of decomposition of a 1:1 mixture of acetone-$d_6$ and ethane.

Some $CH_3$ radicals apparently are produced in this system and scrambling ($CH_2D_2$) is evident. A strong deuterium bias in the methane is observed, indicating that $C_2H_6$ is not undergoing extensive decomposition to methyl radicals. The hydrogen fraction is relatively nonbiased and gives

$$[HD]^2/([H_2][D_2]) = 5$$

in fair agreement with the classical equilibrium constant of 4 expected from an atomic mechanism.

*c. Acetone-$d_6$ + $(CH_3)_2N_2$ Mixture.* Table IX gives isotopic analyses for decomposition of a 1:1 mixture of acetone-$d_6$ + $(CH_3)_2N_2$. The $(CH_3)_2N_2$ alone (10 torr) showed no decomposition when irradiated neat but in admixture with acetone-$d_6$ reacts to produce methane with a strong H bias. Scrambling is again observed. No strong bias is found in the hydrogen and $[HD]^2/([H_2][D_2]) = 3.6$, indicating an atomic mechanism for hydrogen formation.

*d. Acetone-$d_6$ + Cyclopropane Mixture.* Table X gives isotopic analyses for a mixture of acetone-$d_6$ and cyclopropane.

No methane derived from $CH_3$ is produced and the scrambling ($CH_2D_2$) is quite small. Evidently no H atoms are produced since $H_2$ is absent. Clearly, however, D atoms are involved.

*e. Effect of Acetone-$d_6$ Pressure and of Acetone Pressure on Total Yield.* Figure 4 shows that the total yield

TABLE VIII: Methane and Hydrogen Analysis in Decomposition of a Mixture of 10 torr of $CD_3COCD_3$ + 10 torr of $C_2H_6$

| | methane | | | | | hydrogen | | |
|---|---|---|---|---|---|---|---|---|
| product species | $CD_4$ | $CD_3H$ | $CH_2D_2$ | $CH_3D$ | $CH_4$ | $D_2$ | HD | $H_2$ |
| mol % | 38.2 | 43.3 | 12.2 | 2.9 | 3.4 | 25.9 | 52.9 | 21.2 |

TABLE IX: Methane and Hydrogen Analysis in Decomposition of a Mixture of 9 torr of Acetone-$d_6$ and 9 torr of $(CH_3)_2N_2$

| | methane | | | | | hydrogen | | |
|---|---|---|---|---|---|---|---|---|
| species | $CD_4$ | $CD_3H$ | $CH_2D_2$ | $CH_3D$ | $CH_4$ | $D_2$ | HD | $H_2$ |
| mol % | 9.0 | 14.0 | 12.0 | 31.0 | 34.0 | 22.6 | 48.5 | 28.9 |

TABLE X: Methane and Hydrogen Analysis in Decomposition of a Mixture of 20 torr of Acetone-$d_6$ + 5 torr of Cyclopropane

| | methane | | | | hydrogen | | |
|---|---|---|---|---|---|---|---|
| species | $CD_4$ | $CD_3H$ | $CH_2D_2$ | $CH_3D$ + $CH_4$ | $D_2$ | HD | $H_2$ |
| mol % | 66.6 | 28.1 | 5.3 | 0.0 | 62.8 | 36.7 | <1 |

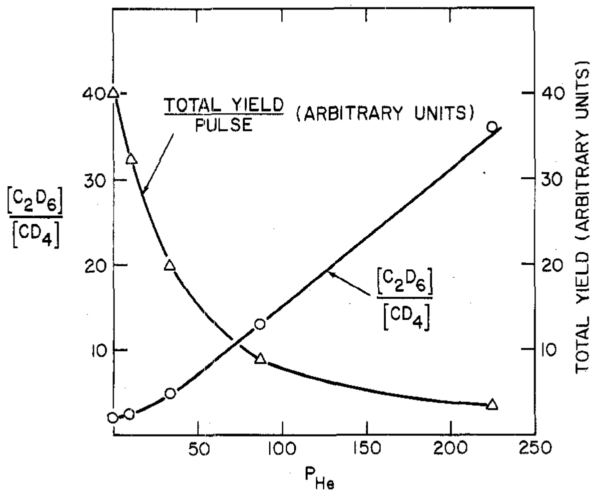


**Figure 5.** Effect of added helium on product ratio $[C_2D_6]/[CD_4]$ in acetone-$d_6$ decomposition.

of hydrocarbon products is proportional to pressure from 2.5 to 80 torr. Further, the figure shows that the total yield is hardly affected by adding to the reaction mixture an amount of acetone equal to that of acetone-$d_6$. It will be recalled (section 4a) that mixtures of acetone and acetone-$d_6$ yield methane whose isotopic composition suggests that acetone is decomposing almost as rapidly as acetone-$d_6$.

*f. Effect of Helium.* Figure 5 shows that added helium increases the product ratio $[C_2D_6]/[CD_4]$ nearly linearly and strongly depresses the total hydrocarbon yield.

## Discussion

Figure 1 shows that acetone is not pumped nearly as efficiently by the P34 laser line as is acetone-$d_6$. The mixture of acetone-$d_6$ and acetone (Figure 4) decomposes at an overall rate suggestive that acetone-$d_6$ is oblivious to the presence of acetone. However, Table VII shows that both are decomposing at roughly equal rates, although a small deuterium bias in the methane is evident. This result shows that energy transfer from $(CD_3)_2CO$ to $(CH_3)_2CO$ must occur at least to populate states of $(CH_3)_2CO$ that are amenable to pumping by the P34 line. The exact mechanism by which the adduct molecule is energized is obscure, although there is evidence for rapid energy transfer during laser photolysis in other systems.[8,9] Figure 5 confirms a single earlier observation[2] that helium effectively quenches the reaction.

The fundamental question to be answered is whether the stationary state mechanism proposed earlier[2] is correct. The failure of $[CD_4]/[CO]$ and $[CD_4]/[C_2D_6]$ to rise above unity excludes a long chain mechanism from consideration. Even so, reactions 1–3 could proceed, at least during the laser pulse with the methyl radical concentration relatively stationary. However, the observation (Table II) that hydrogen and ethylene are major reaction products mitigate against anything as simplistic as reactions 1–3 to explain the chemistry. The isotopic distributions of the methane and hydrogen fractions clearly exclude molecular elimination as major primary processes. Thus, reactions like (11) and (12) may be dismissed. Although hydrogen atom

$$CH_3COCH_3 \rightarrow CH_4 + CH_2CO \qquad (11)$$

$$CH_3COCH_3 \rightarrow H_2 + CH_2CO + CH_2 \qquad (12)$$

production could result from a primary process such as reaction 13, there is no compelling reason to prefer this

$$CH_3COCH_3 \rightarrow H + CH_2COCH_3 \qquad (13)$$

process to reaction 1, especially since reaction 1 is the only known primary process in the thermal decomposition of acetone. If reaction 1 is the sole primary process, hydrogen and ethylene in the reaction products must be explained.

*1. The Ketene Mechanism.* An obvious source of ethylene involves reaction 2 followed by decomposition of ketene in reaction 14. Such a mechanism would provide

$$CH_2CO \rightarrow CH_2 + CO \qquad (14)$$

an abundance of $CH_3$ and $CH_2$. The following reactions[10–12] involving these species may be expected to occur in addition to reaction 3:

$$CH_3 + CH_2 \rightarrow H + C_2H_4 \qquad (15)$$

$$CH_2 + CH_2 \rightarrow C_2H_2 + H_2 \text{ (or 2H)} \qquad (16)$$

This mechanism accounts qualitatively for methane, ethane, ethylene, acetylene, and hydrogen and for the isotopic scrambling in the hydrogen and methane. The apparent absence of ketene, corroborated by the material balance experiments (Table II), suggests either that ketene formation is not involved or that its decomposition is total. For the purpose of the present discussion, complete decomposition of ketene is assumed. According to the mechanism under consideration, we believe that only reactions 2, 15, and 16 are involved in production of ethane, ethylene, and acetylene.

$$\frac{[C_2H_2]}{[C_2H_4]} = \frac{k_{16}[CH_2]}{k_{15}[CH_3]} \qquad (17)$$

$$\frac{[C_2H_6]}{[C_2H_4]} = \frac{k_2[CH_3][M]}{k_{15}[CH_2]} \qquad (18)$$

$$\frac{[C_2H_2]\,[C_2H_6]}{[C_2H_4]\,[C_2H_4]} = \frac{k_{16}k_2[M]}{k_{15}^2} \qquad (19)$$

The left-hand side of eq 19 should be proportional to the acetone-$d_6$ pressure, [M]. The data in Table I shows the left-hand side to be 0.44 at 5 torr and 0.35 at 20 torr and, therefore, apparently in conflict with eq 19. However, the precision of the $[C_2H_2]$ measurement at 5 torr is so poor that the ketene mechanism cannot be either dismissed or confirmed on the basis of eq 19 alone.

The ketene mechanism which requires that $CD_3$ radicals attack the parent molecule suggests they also attack an adduct molecule when present. As indicated in the Experimental Section, the results in Table IV are compatible with a kinetic scheme involving abstraction of H and D from the adduct and the parent acetone-$d_6$ for the adducts ethane and acetone, but not cyclopropane. Neither are the results in Table V in which $(CH_3)_2N_2$ is the adduct compatible with such a scheme. A decisive argument against the ketene mechanism results from the examination of the time scale in which the chemistry must take place. The ketene mechanism requires that (a) the ketene is formed during the laser pulse and is decomposed by multiphoton absorption or (b) the ketene formed in the laser pulse or later must decompose thermally before the chemistry is turned off by the drop in temperature following the laser pulse. The first question that must be examined is the time needed to produce ketene, given the optimum conditions of $[CD_3] = [(CD_3)_2CO]$. At a concentration corresponding to 10 torr of $(CD_3)_2CO$ at room temperature, the rate[13] of disappearance of $CD_3$ in reaction 2 is

$$d[CD_3]/dt = -3.55 \times 10^{10}T^{1/2} \exp(-11300/RT)[CD_3][5.9 \times 10^{-7}] \quad (20)$$

If $T = 2000$ K as suggested in preliminary computer modeling, then

$$-d[CD_3]/[CD_3] = (5.5 \times 10^4)\ dt \quad (21)$$

and less than 1% of the methyl radicals could react in reaction 2 in 0.1 μs (approximate pulse time) if that were the only reaction of $CD_3$. Clearly, the reaction of $CD_3$ with acetone-$d_6$ cannot take place during the laser pulse and the ketene cannot, therefore, be subject to multiphoton pumping during that pulse. The length of time between pulses (1.5 s) is so great that the possibility of ketene decomposition in later pulses may be dismissed. If it is assumed that ketene is formed during the laser pulse in spite of this argument, the next question is what is the likelihood of its decomposition in a purely thermal reaction following the laser pulse? This question may be answered by using the rate constant for ketene decomposition of $k = 10^{13.8} \exp(-81000/RT)$ at the prevailing pressure.[14] The result is that a negligible fraction of the ketene can decompose at 2000 K even in tens of microseconds, and only a small fraction in several hundreds of microseconds. By this time the chemistry has been completely arrested as found in more detailed modeling studies. It must be concluded that the experimental evidence suggesting the absence of ketene also constitutes evidence that ketene is never formed in the reaction and that $CD_2$ is never formed in the reaction.

This conclusion is corroborated by the experiment on the decomposition of acetone-$d_6$ in the presence of cyclopropane. Deuterium atoms must be the source of HD in this experiment since the absence of $H_2$ excludes the possibility of the participation of H atoms. The products HD and $D_2$ are formed by reactions 22 and 23. The

$$D + RD \rightarrow D_2 + R \quad (22)$$

$$D + RH \rightarrow HD + R' \quad (23)$$

relative rate constants for reactions 22 and 23 are not known, but the activation energy difference may be estimated to be about the same as $E_4 - E_2 \sim 1.8$ kcal mol$^{-1}$. At 2000 K, this would give $[HD]/[D_2] \simeq 0.6$ in agreement with the observed ratio. This result does not prove, but is suggestive that, reaction 16 is not an important source of hydrogen relative to reaction 22. The ketene mechanism is weakened by this observation and by the observation that abstraction of H from $(CH_3)_2N_2$ by $CD_3$ is much easier than the known rate constant requires. When these results are coupled with the excellent material balance (Table II) and the kinetic arguments suggesting the absence of ketene and of $CD_2$, a search for an alternative reaction mechanism is mandated.

*2. The Ethane Mechanism.* Among the more striking results are those summarized in Tables V and IX on reactions involving the adduct $(CH_3)_2N_2$. Even though neat $(CH_3)_2N_2$ is unaffected by the laser radiation, in admixture with $(CD_3)_2CO$ it decomposes more rapidly than the latter. This does not prove, but is suggestive of, a high temperature being developed during or immediately following the laser pulse. Further, the hydrogen in $(CH_3)_2N_2$ is either far easier to remove by abstraction than the known kinetics would indicate or deuterium is *not* abstracted from acetone-$d_6$, but from another molecule with a stronger C–D bond. If the ketene mechanism is to be rejected, no $CD_2$ is involved and reaction 15 cannot be invoked to explain the abundant hydrogen atoms and ethylene in the reaction products. These difficulties can all be circumvented by a mechanism involving the following: (a) nearly total decomposition of acetone-$d_6$ by reaction 1 near the focus (~1 mm$^3$) to produce CO and $2CD_3$ in relatively cold condition; (b) a very rapid rise in temperature caused by recombination of $CD_3$ radicals in reaction 3; (c) the subsequent chemistry is that of the thermal decomposition of ethane at the temperature generated by reaction 3. Carbon monoxide is considered to be an inert gas. The ethane mechanism has the following virtues with respect to the experimental observations.

(1) Any adduct that has the potential to form methyl radicals or ethane should, in the first approximation, exhibit the same deuterium isotope effect ($[CD_3H]/[CD_4]$) since that ratio is formed by reactions 5 and 7 in such cases. Thus, mixtures of acetone-$d_6$ with acetone, $(CH_3)_2N_2$, or $C_2H_6$ which show similar results (Tables IV and V) are explained. Further, the ratio $[CD_3H]/[CD_4]$ for the adduct cyclopropane is formed from reactions 4 and 7 which gives a calculated ratio at 2000 K of 0.26, a result within experimental error of the observed ratio of 0.40. Rapid formation of propylene by pyrolysis of cyclopropane may also tend to raise the observed ratio because of the more labile H in propylene.

(2) Methane, ethylene, and hydrogen are known to be products of the pyrolysis of ethane (reactions 24–26). The

$$M + C_2H_6 \rightarrow 2CH_3 + M \quad (24)$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \quad (25)$$

$$C_2H_5 + M \rightarrow C_2H_4 + H + M \quad (26)$$

chains are propagated by reaction 25 and 27 and termi-

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \quad (27)$$

nated by reaction 28 (reactions requiring third bodies may be neglected).

$$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4 \quad (28)$$

(3) If the temperature is high enough, acetylene will be formed by decomposition of ethylene.

$$H + C_2H_4 \rightarrow H_2 + C_2H_3 \quad (29)$$

$$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3 \quad (30)$$

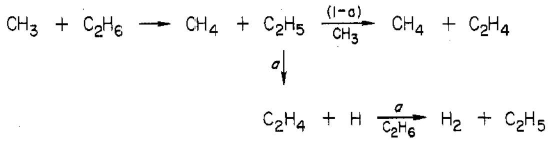
$$C_2H_3 \rightarrow H + C_2H_2 \quad (31)$$

(4) During the laser pulse, energy can be transferred to an adduct which may or may not undergo concurrent multiphoton dissociation. The adduct $(CH_3)_2N_2$ decomposes more rapidly than acetone-$d_6$, acetone slightly less rapidly. $C_2H_6$ decomposes far more slowly. The degree to which an adduct "keeps up" with the acetone-$d_6$ is signaled by the deuterium biases in the products. This diagnostic may prove to be quite useful in understanding energy transfer in complex chemical systems at high temperatures.

(5) The temperature can be calculated from the thermochemistry of reaction 3 and the heat capacities of the various species present. Such model calculations have been carried out and suggest temperatures approaching ~1900 K.

(6) The kinetics of ethane decomposition are sufficiently well understood to enable us to predict the distribution of reaction products as a function of time. This modeling has been done and is the subject of a paper in preparation.

The insensitivity of the product ratio $[C_2H_4]/[CH_4]$ to changes in pressure of acetone is especially interesting since this places certain constraints on the ethane mechanism which may be written by eq 32 for methane and ethane



$$\begin{tikzcd} CH_3 + C_2H_6 \arrow[r] & CH_4 + C_2H_5 \arrow[r, "(1-a)", "CH_3"'] \arrow[d, "a"'] & CH_4 + C_2H_4 \\ & C_2H_4 + H \arrow[r, "a", "C_2H_6"'] & H_2 + C_2H_5 \end{tikzcd} \qquad (32)$$

accounting purposes. The branching ratio determines the product ratio $[C_2H_4]/[CH_4]$. The relative amount of $CH_4$ produced may be represented by the power series in eq 33.

$$[CH_4] = 1 + (1 - a) + a(1 - a) + a^2(1 - a) + ... \qquad (33)$$

Correspondingly, ethylene is represented by eq 34. It

$$[C_2H_4] = 1 + a + a^2 + a^3 + ... \qquad (34)$$

follows that

$$[CH_4] = 2 \qquad (35)$$

$$[C_2H_4] = (1 - a)^{-1} \qquad (36)$$

Thus, $[C_2H_4]/[CH_4]$ is given by

$$[C_2H_4]/[CH_4] = 0.5(1 - a)^{-1} \qquad (37)$$

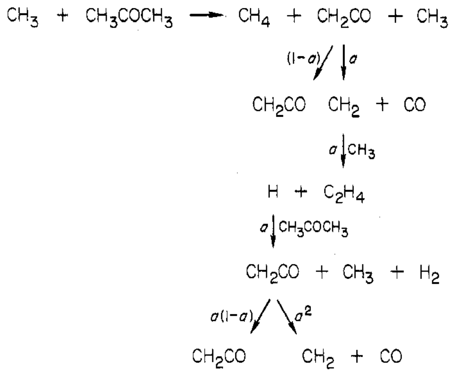
If the branching ratio, $a$, is very small (very little decomposition of $C_2H_5$), $[C_2H_4]/[CH_4]$ approaches 0.5. As $a$ approaches unity, $[C_2H_4]/[CH_4]$ rises assymptotically toward infinity. The experimentally found ratio $[C_2H_4]/[CH_4] \sim 1$ (Table IV) requires that $a \sim 0.5$. Any more detailed discussion of this result is best deferred until the computer modeling work is presented. It can be said, however, that a branching ratio of $a = 0.5$ is quite consistent with the kinetics of ethyl radical decomposition and reaction with methyl if the temperature is around 1900 K, i.e., about half the ethyl radicals decompose and half react with $CH_3$.

An estimate of the maximum temperature can be made since the product ratio, $[C_2H_4]/[CH_4] \sim 1$, requires that $a \sim 0.5$ which demands that

$$k_{26} = k_{28}[CH_3] \qquad (38)$$

The maximum possible value of $[CH_3]$ is twice the initial acetone concentration. Thus, the maximum temperature is defined uniquely by eq 38. Using a value of $k_{26}$ of one tenth its value at the high pressure limit,[15] and assuming the value of $k_{28}$ of 0.06 times the recombination rate constant for methyl radicals,[15] we calculate a peak temperature of 1800 K.

It is of interest to examine the constraints placed upon the ketene mechanism by the experimental observation that $[C_2H_4]/[CH_4] \sim 1$. The fraction, $a$, of the ketene initially formed would decompose as indicated in eq 39. The product ratio $[C_2H_4]/[CH_4] = a(1 - a)^{-1}$. Thus, the observed product ratio of $\sim$1 requires $a \sim 0.5$, i.e., one-half the ketene must dissociate. However, it has already been argued (discussion section 1) that 1900 K is far too low a temperature for ketene to decompose to this extent in the estimated time available. The very high temperature required to produce effective dissociation of ketene is so great that the much less stable acetone molecule could not survive long enough to sustain the mechanism. This constitutes a reducto ad absurdum argument against the ketene mechanism.



$$\begin{tikzcd} CH_3 + CH_3COCH_3 \arrow[r] & CH_4 + CH_2CO + CH_3 \arrow[dl, "(1-a)"'] \arrow[d, "a"] & \\ CH_2CO & CH_2 + CO \arrow[d, "a"', "CH_3"] & \\ & H + C_2H_4 \arrow[d, "a"', "CH_3COCH_3"] & \\ & CH_2CO + CH_3 + H_2 \arrow[dl, "a(1-a)"'] \arrow[d, "a^2"] & \\ CH_2CO & CH_2 + CO & \end{tikzcd} \qquad (39)$$

The data in Figure 5 suggest that helium not only retards the pumping process but also lowers the temperature and, as a consequence, increases the ethane/methane ratio. Whether the temperature is lowered by added helium or by a lowered rate of energy deposition (low acetone-$d_6$ pressure), the result is to raise the ethane/methane product ratio. Another indicator that lowered acetone-$d_6$ pressure lowers the temperature is the effect of pressure on the acetylene yield (Figure 2). It is suggested that acetylene is generated by thermal decomposition in reaction 31 of the vinyl radical formed in reactions 29 and 30.

Evidently, the decomposition of an adduct molecule proceeds approximately in accord with its thermal stability as though energy transfer is efficient, but rupture of a bond stronger than $CD_3$–$COCD_3$ is especially difficult ($CH_3$–$CH_3$). Rupture of a bond weaker than $CD_3$–$COCD_3$ is rapid ($CH_3$–$N_2CH_3$) and a bond of about the same energy ruptures at about the same rate ($CH_3$–$COCH_3$).

## References and Notes

(1) The unit of wavelength used in this paper is micron (μm) defined as $10^{-6}$ m. The pressure unit used is torr where 1 torr is 133.322 N $m^{-2}$. The second-order rate constant unit used is $mol^{-1}$ $cm^3$ $s^{-1}$ where 1 $cm^3$ is equal to $10^{-6}$ $m^3$.
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