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IR LASER-INDUCED DECOMPOSITION OF DIETHYL KETONE AND *n*-BUTANE*

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Summary

The focused IR laser-induced decomposition of diethyl ketone was studied and compared with the SiF_4-sensitized decomposition of diethyl ketone and *n*-butane. A model was constructed for the direct decomposition of diethyl ketone involving total decomposition of diethyl ketone into ethyl radicals and carbon monoxide near the focus. The reaction between ethyl radicals forms a short-lived *n*-butane which decomposes statistically into two ethyls or two methyls and ethylene. The system is allowed to react and due account is taken of unimolecular fall-off behavior for all species. The temperature which best explains the experimental product distribution is 1400 K. SiF_4-sensitized decompositions of diethyl ketone and *n*-butane appear to be characterized by purely thermal processes.

1. Introduction

The chemistry of acetone-d_6 induced by a focused CO_2 TEA laser tuned to the P 34 line at 9.68 μm is triggered by nearly total decomposition of the acetone-d_6 in a small volume near the focus [1]. The "temperature" of the resulting methyl radicals is not well defined because thermal equilibrium is not established at the outset. Acetone-d_6 was chosen for the study since it absorbs much more strongly than acetone at the P 34 line:

$$CD_3COCD_3 \rightarrow 2CD_3 + CO \qquad (1)$$

Recombination of CD_3 radicals is the only reaction immediately following the initial dissociation

$$CD_3 + CD_3 + M \rightarrow C_2D_6 + M \qquad (2)$$

and thermal equilibrium is established by means of V → T energy transfer in methyl radical association. The temperature rises quickly to about 1900 K, causing a rapid expansion of the gas. The subsequent chemistry, the thermal decom-

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position of C_2D_6, which is controlled by hydrodynamic gas flow, energy transfer and thermal conductivity has been modeled by Peterson *et al.* [2].

Another ketone whose conventional chemistry is reasonably well understood is diethyl ketone. In this case, decomposition should occur initially by a process analogous to that for acetone:

$$CH_3CH_2COCH_2CH_3 \rightarrow 2CH_3CH_2 + CO \qquad (3)$$

Reactions of the ethyl radicals would cause the temperature to rise. On the assumption that recombination of C_2H_5 dominates disproportionation, the reaction that generates temperature is

$$2CH_3CH_2 + M \rightarrow n\text{-}C_4H_{10} + M \qquad (4)$$

The high temperature chemistry occurring near the focus should be understandable in its gross features by analogy with acetone decomposition. Just as acetone at the laser focus behaves as though it were ethane, diethyl ketone should behave as though it were *n*-butane. Reaction product distributions have been examined using a focused laser on diethyl ketone neat and sensitized with SiF_4 and on *n*-butane sensitized with SiF_4.

2. Experimental details

A pulsed (0.6 Hz) TEA laser was used in all experiments. The energy of the beam was about 0.8 J per pulse at 9.68 μm. A Pyrex reaction cell 2.5 cm in diameter and 6 cm long with sodium chloride windows at each end was used. In focused experiments a sodium chloride lens with a focal length of 5 cm was placed immediately at the front cell window. Two mildly focusing mirrors reduced the beam diameter to less than the lens diameter. After exposure to the laser beam, about one-quarter of the cell contents were directed to a gas chromatograph with an appropriate valving system. The columns used were Poropak Q which resolved methane, ethane, ethylene, acetylene, propane and the unresolved pair propylene–*n*-butane. The resolution of propylene and *n*-butane was achieved in some experiments using a Porasil C column. Flame ionization detection was employed. Material balance experiments were carried out by a combination of mass spectrometry (to measure hydrogen, carbon monoxide and methane) and gas chromatography (for hydrocarbons); the two analyses were linked by the common constituent methane.

3. Results

3.1. Decomposition of neat diethyl ketone

The total product yield per pulse as measured by the sum of the chromatographic areas is closely proportional to the diethyl ketone pressure, as shown in Fig. 1. The number of pulses varied from one at the higher pressures to 20 at the lowest pressure. At 10 Torr, the yield per pulse was the same with one pulse as

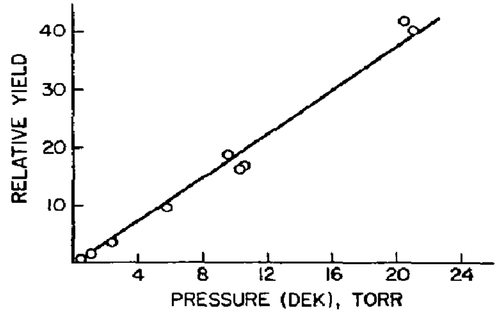

Fig. 1. The relationship between the total product yield per pulse and the diethyl ketone pressure (decomposition of neat diethyl ketone).

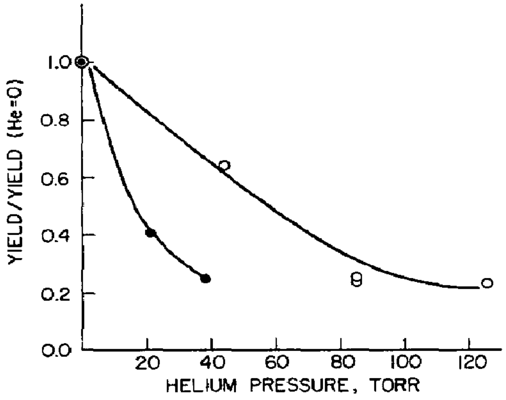

Fig. 2. The relationship between the total product yield per pulse and the helium pressure: ○, P_{DEK} = 10 Torr; ●, P_{DEK} = 0.6 Torr.

TABLE 1

Product yields in the decomposition of 10.3 Torr of diethyl ketone

Product	*Proportion of product* (mol. %)
CO	29
H_2	10
CH_4	6.7
C_2H_6	8.2
C_2H_4	32
C_3H_8	5.0
C_2H_2	5.9
C_3H_6	0.88
C_4H_{10}	1.7

with five. The material balance is reported in Table 1 for the decomposition of 9.8 Torr of diethyl ketone.

The empirical formula obtained from the data in Table 1 is $C_{5.3}H_{10.3}O_{1.00}$. A duplicate experiment gave $C_{5.0}H_{10.2}O_{1.00}$. These results are in good agreement with the formula for diethyl ketone.

Figure 2 shows the effect of helium on the total yield per pulse. As noted in the decomposition of acetone-d_6 [2], helium effectively quenches the reaction.

TABLE 2

Relative yields of products in the SiF_4-sensitized decomposition of 2.5 Torr of acetone-d_6

Product	*SiF_4 pressure* (Torr)					
	0	*10*	*20*	*20*	*20*	*20*
	Relative fluence F					
	1.0	*1.0*	*1.0*	*0.4*	*0.25*	*0.13*
C_2D_6	1.0	1.0	1.0	1.0	1.0	1.0
CD_4	0.016	0.33	0.78	0.31	0.28	0.05
C_2D_4	0.014	0.29	0.66	0.31	0.27	0.06
C_3D_8	0.02	0.02	0.03	0.015	0.014	ND[a]
C_2D_2	<0.01	0.19	0.31	0.12	0.06	ND
Total yield per pulse	—	—	1.0	0.17	0.092	0.0087

[a] ND, not detected.

3.2. *Sensitization by SiF_4*

3.2.1. *Acetone-d_6*

Several experiments were carried out using SiF_4 to sensitize the decomposition of acetone-d_6 in order to compare the product distributions with those obtained in the unsensitized decomposition. The distribution of hydrocarbon products is presented in Table 2 as a function of the fluence and of the SiF_4 pressure. Increasing the fluence or the SiF_4 pressure increases the apparent temperature; this is reflected by substantially increased yields of methane, ethylene and acetylene. The total yield per pulse is approximately proportional to the square of the fluence.

3.2.2. *SiF_4-sensitized decompositions of diethyl ketone and n-butane*

A comparison between the SiF_4-sensitized and the unsensitized diethyl ketone decomposition is presented in Table 3. The hydrocarbon products of the decomposition of diethyl ketone sensitized by SiF_4 are compared in Table 4 with the products of the SiF_4-sensitized decomposition of *n*-butane. The SiF_4-sensitized decomposition of 0.5 Torr of *n*-butane shows a product distribution very similar to that obtained in the sensitized decomposition of diethyl ketone.

The relative total yield per pulse as a function of fluence for diethyl ketone decomposition is given in Table 5. Although the precision of the data is poor, the yield as in the case of acetone-d_6 is approximately proportional to the square of the fluence.

Figure 3 shows the effect of changing the SiF_4 pressure on the total product yield in the SiF_4-sensitized decomposition of 2.5 Torr of *n*-butane. The yield per pulse is approximately proportional to the square of the SiF_4 pressure. Experiments in which the *n*-butane pressure was varied from 3 to 42 Torr at 2.5 Torr

TABLE 3

Product distribution in the unsensitized and SiF_4-sensitized decomposition of 0.5 Torr of diethyl ketone

Product	*Relative proportions of the products under the following SiF_4 pressures*	
	0 Torr	*19 Torr*
C_2H_6	0.47	0.18
CH_4	$\approx$0.00	0.10
C_2H_4	1.00	1.00
C_3H_8	0.71	0.052
C_2H_2	0.065	0.16
C_4H_{10}	0.40	0.015

TABLE 4

Comparison between the products of the SiF_4(20 Torr)-sensitized decomposition of 0.5 Torr of diethyl ketone and 0.5 Torr of *n*-butane

Product	*Relative proportions of the products of the following hydrocarbons*	
	Diethyl ketone	*n-Butane*
C_2H_4	1.00	1.00
CH_4	0.10	0.12
C_2H_6	0.18	0.20
C_3H_8	0.05	0.02
C_2H_2	0.16	0.28
C_4H_{10}	0.02	—

TABLE 5

Relative total yield per pulse as a function of fluence[a] in diethyl ketone decomposition

Relative fluence	*Relative yield per pulse*
1.0	1.0
0.40	0.12
0.25	0.13

[a] 0.1 Torr of diethyl ketone; 20 Torr of SiF_4.

of SiF_4 showed no significant variations in the total yield with *n*-butane pressure. Increasing the *n*-butane pressure elevates the temperature, however, since the methane yield rises and the ethane yield falls.

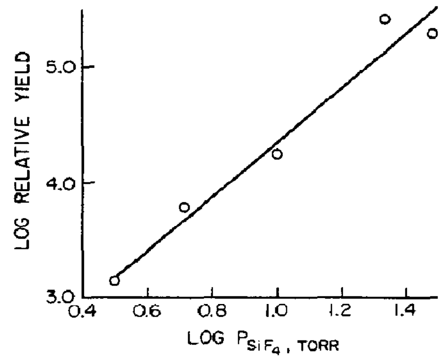

Fig. 3. The relationship between the total relative product yield per pulse and the pressure of the SiF_4 sensitizer in the decomposition of *n*-butane (slope, 2.3; yield, $C_3[SiF_4]^{2.3}$).

4. Discussion

As in the case of acetone decomposition, the amount of reaction per pulse is proportional to the pressure. The net effect of reducing the pressure in focused geometry is to reduce the number of molecules that are subjected to the critical fluence required for dissociation. Thus, it is not surprising that the yield per pulse is proportional to the pressure. The effect of adding helium, as in the case of acetone-d_6 decomposition, is to suppress reaction by an effective reduction in the temperature (Fig. 2).

It has been argued that the laser-induced decomposition of acetone in focused geometry results in total decomposition into methyl radicals and carbon monoxide near the focus. The subsequent chemistry is understandable on the basis of known methyl radical chemistry. In particular, the participation of acetone in the chemistry after the laser pulse was rejected mainly on the basis of the demonstrated absence of ketene. If diethyl ketone participates in a free-radical chain reaction, ethyl radicals may be expected preferentially to attack the α position of the ketone to produce the precursor of methyl ketene:

$$C_2H_5 + CH_3CH_2COCH_2CH_3 \rightarrow C_2H_6 + CH_3CHCOCH_2CH_3 \quad (5)$$

$$CH_3CHCOCH_2CH_3 \rightarrow CH_3CH{=}CO + C_2H_5 \quad (6)$$

Methyl ketene was not detected in the products of diethyl ketone decomposition. The possibility that methyl ketene is formed in reaction (6) but reacts rapidly with C_2H_5 to form *sec*-butyl may be dismissed since propylene, the expected product of the decomposition of *sec*-butyl, is never present in substantial quantities. If methyl ketene were produced but not detected, the observed material balance would be upset severely. The very good material balance observed argues against the presence of undetected methyl ketene and therefore against a chain reaction involving reactions (5) and (6).

A fairly evident *a priori* model, based on the acetone analogy [1], suggests that the ethyl radicals formed in reaction (3) generate temperature by recombination in reaction (4). The chemistry that follows should closely approximate the thermal decomposition of *n*-butane. As Benson [3] has pointed out, the product distribution in the chain decomposition of *n*-butane may be predicted quantitatively by considering the propagation steps only:

$$\mathrm{R} + n\text{-}\mathrm{C_4H_{10}} \rightarrow \mathrm{RH} + p\text{-}\mathrm{C_4H_9} \tag{7}$$

$$p\text{-}\mathrm{C_4H_9} \rightarrow \mathrm{C_2H_4} + \mathrm{C_2H_5} \tag{8}$$

At very high temperatures, C_2H_5 may be expected to decompose rather efficiently:

$$\mathrm{C_2H_5} \rightarrow \mathrm{H} + \mathrm{C_2H_4} \tag{9}$$

Thus, at most two C_2H_4 molecules result from one reaction (7). The secondary H of *n*-butane is also attacked:

$$\mathrm{R} + n\text{-}\mathrm{C_4H_{10}} \rightarrow \mathrm{RH} + sec\text{-}\mathrm{C_4H_9} \tag{10}$$

$$sec\text{-}\mathrm{C_4H_9} \rightarrow \mathrm{CH_3} + \mathrm{C_3H_6} \tag{11}$$

The ratio of ethylene to propylene in the reaction products is given by

$$\frac{[\mathrm{C_2H_4}]}{[\mathrm{C_3H_6}]} \leq \frac{2k_7}{k_{10}} \leq 2\exp\left(-\frac{1800}{RT}\right) \tag{12}$$

At 2000 K, $[C_2H_4]/[C_3H_6]$ should be 1.3 or less. At any temperature, $[C_2H_4]/[C_3H_6]$ should not exceed 2.0. Table 1 shows that there is thirty times more ethylene than propylene and a severe perturbation on the classical chain mechanism must exist.

The marked elevation of the ratio of ethylene to propylene may be the result of optical pumping of ethyl radicals formed in their quasi-continua in a primary process such as those reported by Lee *et al.* [4]. This could result in nearly total dissociation of ethyl into H + C_2H_4. Other non-thermal processes may also be responsible for the elevated ratio of ethylene to propylene. Since the simplest non-thermal behavior is unimolecular fall-off it is necessary to examine the effect on the chemistry of the fall-off characteristics of reactions such as (8) and (11).

4.1. Calculation of unimolecular fall-off behavior

Preliminary calculations of fall-off behavior for reaction (11) suggested that a first-order rate constant with a value of about 10^{-5} of the limiting high pressure value is to be expected at about 1900 K. It became evident that any attempt to assess the validity of a chemical model would have to take proper account of the fall-off behavior of all unimolecular decompositions and of the corresponding recombinations and additions to olefinic π bonds. Since fall-off behavior has not been measured experimentally for the vast majority of the species of interest in a model involving the high temperature chemistry of ethyl radicals, it was necessary to seek a reasonably simple prescription for the calculation of the fall-off behavior. The formalism of Troe [5] was adopted. Our use of this treatment is described here for the unimolecular reaction

$$A + M \rightarrow \text{products} + M \tag{13}$$

The strong collision rate constant k_0^{sc} is modified by a weak collision factor β_c (less than unity) which lowers the strong collision rate constant to k_0. The high pressure rate constant k_∞ and k_0 represent the limiting high and low pressure first-order rate constants. The true first-order rate constant is then calculated and is asymptotic to the two limiting cases. A test of the procedure gave good agreement with the experimental fall-off curve for ethane decomposition at 873 K [6].

4.1.1. Calculation of k_0^{sc}

The Troe prescription defines k_0^{sc} in terms of the concentration [M], the Lennard-Jones collision frequency Z_{LJ}, the vibrational partition function Q_{vib}, the harmonic oscillator density of states $\varrho_{vib,h}$ and the activation energy E_0:

$$k_0^{sc} = [M]Z_{LJ}\left(\varrho_{vib,h}\frac{E_0kT}{Q_{vib}}\right)\exp\left(-\frac{E_0}{kT}\right)F_{anh}F_E F_{ri} F_{rot} F_{corr} \tag{14}$$

The factor F_{anh} is the anharmonicity correction, F_E takes account of the energy dependence of the density of states, F_{ri} is the internal rotor correction factor, F_{rot} refers to the external rotational contribution and F_{corr} is a factor which corrects for small coupling contributions. Lennard-Jones well depths and collision diameters were obtained from published values [7] for the specific compounds or were estimates from data on closely related compounds. In the calculation of the vibrational partition function, vibrational frequencies were taken directly from the literature [8] for stable molecules and from the estimates of Rabinovitch and Setser [9] for free radicals. The F factors were evaluated according to Troe's prescription.

4.1.2. Evaluation of β_c

The expression for β_c given by

$$\frac{\beta_c}{1-\beta_c^{1/2}} = -\frac{\langle \Delta E \rangle}{F_E kT} \tag{15}$$

has one major difficulty: the estimation of the average energy $-\langle \Delta E \rangle$ transferred per collision from a highly excited molecule to its collision partner. Almost no direct experimental information exists on $-\langle \Delta E \rangle$ and we adopted the practice of using $-\langle \Delta E \rangle = 10$ kJ mol^{-1} collision^{-1} based on experimental data on energy transfer from excited cycloheptatriene to various collision partners [10]. The following equation is solved for β_c and k_0 is obtained:

$$k_0 = \beta_c k_0^{sc} \tag{16}$$

4.1.3. Evaluation of k_{1st}

The value of k_∞ is given by the Arrhenius expression

$$k_\infty = A \exp\left(-\frac{E_0}{kT}\right) \tag{17}$$

Then

$$\frac{k_{1st}}{k_\infty} = F^{\mathrm{LH}}\left(\frac{k_0}{k_\infty}\right) F^{\mathrm{sc}}\left(\frac{k_0}{k_\infty}\right) F^{\mathrm{wc}}\left(\frac{k_0}{k_\infty}\right) \tag{18}$$

The first-order rate constant in the fall-off region, k_{1st} in eqn. (18), is obtained by using the value of k_0 calculated above from eqn. (16) and the experimental value of k_∞. The term F^{LH} is the Lindemann–Hinshelwood factor defined by

$$F^{\mathrm{LH}} = \frac{k_0/k_\infty}{1 + k_0/k_\infty} \tag{19}$$

The modifying factors $F^{\mathrm{sc}}(k_0/k_\infty)$ and $F^{\mathrm{wc}}(k_0/k_\infty)$ are obtained as follows. The strong collision factor F^{sc} according to Troe is given approximately by

$$\log F^{\mathrm{sc}} \approx -\frac{0.137(S_{\mathrm{K}} - 1)B_{\mathrm{K}}}{1.10(S_{\mathrm{K}} - 1) + B_{\mathrm{K}}} \tag{20}$$

The Kassel parameter B_{K} is given by

$$B_{\mathrm{K}} = \frac{E_0 + a(E_0)E_z}{kT}\,\frac{S_{\mathrm{K}} - 1}{S - 1} \tag{21}$$

where

$$S_{\mathrm{K}} = 1 + \sum_{i=1}^{s} \frac{h\nu_i/kT}{\exp(h\nu_i/kT) - 1} \tag{22}$$

and s is the number of oscillators.

A computer program was written and k_{1st}/k_∞ was calculated for all *n*-alkanes and *n*-alkyl radicals from C_2 to C_4 at several temperatures above those for which fall-off data exist. Among the more striking features of the results is that, at 1300 K and pressures as great as 10^3 Torr, k_{1st}/k_∞ is less than 0.01 for 1-butyl and 2-butyl decompositions while the corresponding value for *n*-butane decomposition is about 0.3. The major cause of this large difference in k_{1st}/k_∞ is that the density of states at the dissociation energy for the butyl radicals is much smaller than that at the dissociation energy for *n*-butane. This effect is greatly magnified at higher temperatures. For example, at 1900 K, k_{1st}/k_∞ for *n*-butane and *n*-butyl decompositions at 10 Torr is 0.009 and 3×10^{-6} respectively. Calculated fall-off becomes so severe at higher temperatures that, at constant pressure, for some species the calculated first-order rate constant actually goes through a maximum and decreases as the temperature is increased.

4.2. *Computer simulation*

High pressure rate constants were taken from the review of Allara and Shaw [11] except for those not listed in the review. Of those not listed, rate constants for the abstraction of H from ethylene and propylene by H and CH_3 and for the addition of H and CH_3 to ethylene and propylene were taken from Trotman-Dickenson and Milne [12]. For all atomic and free-radical cracking reactions, branching ratios were taken to be statistical. First-order rate constants were calculated for a pressure of 10 Torr at temperatures of 1000, 1300, 1500, 1600 and 1900 K using the previously discussed formalism of Troe. The array of 79 differential equations for the rates of the reactions (shown in Appendix A) was solved with a computer without any consideration being given to the physical dynamics involved following the deposition of the laser energy in the small volume near the laser focus. A number of initial conditions and a constant temperature were assumed and the program was then allowed to run. The initial conditions selected included temperature, pressure and the nature of the species present. The results were displayed in terms of moles of stable reaction products relative to the number of moles of carbon monoxide produced. The chemistry was arbitrarily stopped at 100 μs at which time all free radicals had been almost entirely consumed except CH_3. CH_3 radicals were allowed to recombine to form ethane.

4.3. *Initial conditions*

Diethyl ketone in all initializations is assumed to be present at the outset at a pressure of 10 Torr at the isothermal temperature.

The first initialization assumes that the diethyl ketone dissociates entirely into $2C_2H_5 + CO$ (at constant volume) at which point the system is allowed to react isothermally at several temperatures. A second initialization assumes that all C_2H_5 is formed in such a highly excited state that total dissociation into $H + C_2H_4$ occurs. Again the system is allowed to react isothermally. A third initialization allows all ethyl radicals to recombine to form *n*-butane which in turn is allowed to react isothermally. The failure of the first three models to reproduce the distribution of reaction products suggested a fourth initialization. This assumes that the C_2H_5 radicals first formed are sufficiently excited vibrationally that they form a very short-lived *n*-butane which always decomposes by

$$C_4H_{10}^* \rightarrow 2C_2H_5 \tag{23}$$

or by

$$C_4H_{10}^* \rightarrow CH_3 + n\text{-}C_3H_7^* \tag{24}$$

The branching ratio is assumed to be statistical. A further assumption is made that the excitation in the short-lived *n*-butane is so great that all $n\text{-}C_3H_7$ radicals formed in reaction (24) retain enough energy to dissociate with 100% probability:

$$n\text{-}C_3H_7^* \rightarrow CH_3 + C_2H_4 \tag{25}$$

Tables 6 - 9 present the results of the computer simulations using these four initializations.

TABLE 6

Product distribution of diethyl ketone decomposition using an initialization of $2C_2H_5$ + CO

Product	*Experimental relative product distribution*	*Calculated relative product distributions for the following temperatures*			
		1300 K	*1500 K*	*1600 K*	*1900 K*
CO	1.0	1.0	1.0	1.0	1.0
H_2	0.34	0.11	0.43	0.31	0.41
C_2H_4	1.10	0.67	0.83	0.99	0.90
CH_4	0.23	0.11	0.18	0.17	0.23
C_2H_6	0.28	0.39	0.42	0.58	0.54
C_3H_8	0.17	0.23	0.089	0.019	0.00
C_3H_6	0.03	0.10	0.16	0.085	0.04
C_2H_2	0.20	0.02	0.12	0.16	0.37
n-C_4H_{10}	0.06	0.17	0.00	0.00	0.00
C_4H_8	ND[a]	0.02	0.07	0.01	0.00

[a] ND, not detected.

TABLE 7

Product distribution of diethyl ketone decomposition using an initialization of 2H + $2C_2H_4$ + CO

Product	*Experimental relative product distribution*	*Calculated relative product distributions for the following temperatures*	
		1600 K	*1300 K*
CO	1.0	1.0	1.0
H_2	0.34	1.85	2.0
C_2H_4	1.10	0.12	0.50
CH_4	0.23	0.00	0.19
C_2H_6	0.28	0.04	0.07
C_3H_8	0.17	0.00	0.00
C_3H_6	0.03	0.00	0.00
C_2H_2	0.20	1.84	1.25
n-C_4H_{10}	0.06	0.00	0.00
C_4H_8	ND[a]	0.00	0.00

[a] ND, not detected.

The results in Table 6 show that the ratio of ethylene to propylene could only be brought into agreement with experiment if the temperature approached 1400 K in which case the computed propane disappeared and the acetylene rose to a very high figure. The second initialization (Table 7), in which H and C_2H_4 were present, is so badly out of line with experimental results at 1600 and 1300 K that it may be dismissed out of hand. Initialization with n-butane (Table 8) at 1500 K yields far too little propane and a ratio of ethylene to propylene an order of magnitude too small. Lowering the temperature to 1300 K produces far too

TABLE 8

Product distribution of diethyl ketone decomposition using an initialization of n-C_4H_{10} + CO

Product	*Experimental relative product distribution*	*Calculated relative product distributions for the following temperatures*		
		1500 K	*1300 K*	*1900 K*
CO	1.0	1.0	1.0	1.00
H_2	0.34	0.39	0.026	0.54
C_2H_4	1.10	0.63	0.047	0.84
CH_4	0.23	0.12	0.00	0.19
C_2H_6	0.28	0.23	0.01	0.37
C_3H_8	0.17	0.02	0.00	0.00
C_3H_6	0.03	0.19	0.02	0.18
C_2H_2	0.20	0.037	0.00	0.23
n-C_4H_{10}	0.06	0.28	0.94	0.00
C_4H_8	ND[a]	0.06	0.00	0.10

[a] ND, not detected.

TABLE 9

Product distribution of diethyl ketone decomposition using an initialization of 1CO + $0.67C_2H_4$ + $1.33CH_3$ + $0.67C_2H_5$

Product	*Experimental relative product distribution*	*Calculated relative product distributions for the following temperatures*		
		1300 K	*1500 K*	*(1400 K)*[a]
CO	1.0	1.0	1.0	1.0
H_2	0.34	0.11	0.28	(0.20)
C_2H_4	1.10	0.90	0.90	(0.90)
CH_4	0.23	0.11	0.32	(0.22)
C_2H_6	0.28	0.57	0.55	(0.56)
C_3H_8	0.17	0.22	0.043	(0.13)
C_3H_6	0.03	0.03	0.03	(0.03)
C_2H_2	0.20	0.03	0.20	(0.12)
n-C_4H_{10}	0.06	0.03	0.01	(0.02)
C_4H_8	ND[b]	0.00	0.02	(0.01)

[a] Interpolated.
[b] ND, not detected.

little ethylene, hydrogen and propane, while raising the temperature to 1900 K results in a computed propane of zero and a ratio of ethylene to propylene that is still unacceptably small. The important ratio of ethylene to propylene can be brought into agreement with experiment by initializing as indicated in Table 9. Table 9 shows the very substantial sensitivity of acetylene and propane to temperature and allows the adjustment of temperature to achieve the optimum agreement with the experimental product distribution. This temperature is about 1400 K.

If the ethyl radicals formed initially are assumed to be at 300 K and in thermal equilibrium with the heat bath, a calculation can be made to determine the maximum temperature to which the observed reaction products can be raised by means of the exothermicity of the reaction which forms them. This calculation has been carried out and the available exothermicity is far short of that required to achieve 1400 K. At least an additional 20 kcal mol^{-1} is required, *i.e.* for two moles of C_2H_5 and one mole of CO 20 kcal must be present in excess of thermal energy at 300 K. If most of this energy resides in C_2H_5, the incipient *n*-butane formed on recombination of C_2H_5 may contain just enough energy for the sequence of reactions (24) and (25) that form the basis of the initialization.

4.4. *Sensitization with SiF_4*

Computer simulations have not been carried out with SiF_4-sensitized reactions and only a qualitative discussion of the results is possible. Experiments with acetone-d_6 sensitized by SiF_4 (Table 2) showed that SiF_4 sensitization sharply raises the methane, ethylene and acetylene yields, demonstrating that a much higher temperature is thereby produced. When the pressure in the decomposition of neat diethyl ketone is reduced from 10 to 0.5 Torr, the temperature is sharply lowered as indicated by the greatly reduced yields of methane and acetylene (Table 3). Sensitization by SiF_4 sharply increases the temperature as in the case of acetone decomposition. Since acetone decomposition may be described on the basis of the association reactions of methyl radicals followed by the high temperature thermal decomposition of ethane, it may hypothesized that sensitized diethyl ketone decomposition may exhibit similarities to *n*-butane decomposition. The results in Table 4 show that this hypothesis is strongly supported by closely similar product distributions.

Although it was necessary to invoke the sequence (23), (24) and (25) in the direct decomposition of diethyl ketone, it is probably not necessary to do so for SiF_4 sensitization where the energy is transferred by collision to diethyl ketone or *n*-butane.

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Appendix A

Model reactions

Initiation

$C_2H_6 \rightarrow CH_3 + CH_3$
$C_3H_8 \rightarrow CH_3 + C_2H_5$
$C_4H_{10} \rightarrow C_2H_5 + C_2H_5$
$C_4H_{10} \rightarrow CH_3 + \mathit{n}\text{-}C_3H_7$

Radical recombination

$CH_3 + CH_3 \rightarrow C_2H_6$
$CH_3 + C_2H_5 \rightarrow C_3H_8$
$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}$
$CH_3 + \mathit{n}\text{-}C_3H_7 \rightarrow C_4H_{10}$
$CH_3 + \mathit{iso}\text{-}C_3H_7 \rightarrow C_4H_{10}$
$CH_3 + C_3H_5 \rightarrow C_4H_8$

Radical cracking

$H + C_2H_5 \rightarrow 2CH_3$
$H + \mathit{n}\text{-}C_3H_7 \rightarrow CH_3 + C_2H_5$
$H + \mathit{iso}\text{-}C_3H_7 \rightarrow CH_3 + C_2H_5$
$H + 1\text{-}C_4H_9 \rightarrow C_2H_5 + C_2H_5$
$H + 1\text{-}C_4H_9 \rightarrow CH_3 + \mathit{n}\text{-}C_3H_7$
$H + 2\text{-}C_4H_9 \rightarrow CH_3 + \mathit{n}\text{-}C_3H_7$
$H + 2\text{-}C_4H_9 \rightarrow C_2H_5 + C_2H_5$
$CH_3 + \mathit{n}\text{-}C_3H_7 \rightarrow C_2H_5 + C_2H_5$
$C_2H_5 + C_2H_5 \rightarrow CH_3 + \mathit{n}\text{-}C_3H_7$
$C_2H_5 + \mathit{n}\text{-}C_3H_7 \rightarrow CH_3 + 1\text{-}C_4H_9$

Radical decomposition

$C_2H_5 \rightarrow H + C_2H_4$
$\mathit{n}\text{-}C_3H_7 \rightarrow C_2H_5 + CH_3$
$\mathit{n}\text{-}C_3H_7 \rightarrow H + C_3H_6$
$\mathit{iso}\text{-}C_3H_7 \rightarrow H + C_3H_6$
$1\text{-}C_4H_9 \rightarrow C_2H_5 + C_2H_4$
$2\text{-}C_4H_9 \rightarrow CH_3 + C_3H_6$
$C_2H_3 \rightarrow H + C_2H_2$

Disproportionation

$H + C_2H_5 \rightarrow H_2 + C_2H_4$
$H + \mathit{n}\text{-}C_3H_7 \rightarrow H_2 + C_3H_6$
$H + \mathit{iso}\text{-}C_3H_7 \rightarrow H_2 + C_3H_6$
$H + \mathit{iso}\text{-}C_4H_9 \rightarrow H_2 + C_4H_8$
$H + 2\text{-}C_4H_9 \rightarrow H_2 + C_4H_8$
$H + C_2H_3 \rightarrow H_2 + C_2H_2$
$CH_3 + C_2H_5 \rightarrow CH_4 + C_2H_4$
$CH_3 + \mathit{n}\text{-}C_3H_7 \rightarrow CH_4 + C_3H_6$
$CH_3 + \mathit{iso}\text{-}C_3H_7 \rightarrow CH_4 + C_3H_6$
$CH_3 + 1\text{-}C_4H_9 \rightarrow CH_4 + C_4H_8$
$CH_3 + 2\text{-}C_4H_9 \rightarrow CH_4 + C_4H_8$
$CH_3 + C_2H_3 \rightarrow CH_4 + C_2H_2$
$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$
$C_2H_5 + \mathit{n}\text{-}C_3H_7 \rightarrow C_2H_6 + C_3H_6$
$C_2H_5 + \mathit{iso}\text{-}C_3H_7 \rightarrow C_2H_6 + C_3H_6$
$C_2H_5 + 1\text{-}C_4H_9 \rightarrow C_2H_6 + C_4H_8$
$C_2H_5 + 2\text{-}C_4H_9 \rightarrow C_2H_6 + C_4H_8$
$C_2H_5 + C_2H_3 \rightarrow C_2H_6 + C_2H_2$
$C_2H_5 + C_2H_3 \rightarrow C_2H_4 + C_2H_4$
$\mathit{n}\text{-}C_3H_7 + C_2H_5 \rightarrow C_3H_8 + C_2H_4$
$\mathit{iso}\text{-}C_3H_7 + C_2H_5 \rightarrow C_3H_8 + C_2H_4$
$\mathit{iso}\text{-}C_4H_9 + C_2H_5 \rightarrow C_4H_{10} + C_2H_4$
$2\text{-}C_4H_9 + C_2H_5 \rightarrow C_4H_{10} + C_2H_4$

Addition

$H + C_2H_2 \rightarrow C_2H_3$
$H + C_2H_4 \rightarrow C_2H_5$
$H + C_3H_6 \rightarrow n\text{-}C_3H_7$
$H + C_3H_6 \rightarrow iso\text{-}C_3H_7$
$H + C_4H_8 \rightarrow 2\text{-}C_4H_9$
$CH_3 + C_2H_4 \rightarrow n\text{-}C_3H_7$
$CH_3 + C_3H_6 \rightarrow 2\text{-}C_4H_9$

H transfer (metathesis)

$H + C_2H_6 \rightarrow H_2 + C_2H_5$
$H + C_3H_8 \rightarrow H_2 + n\text{-}C_3H_7$
$H + C_3H_8 \rightarrow H_2 + iso\text{-}C_3H_7$
$H + C_4H_{10} \rightarrow H_2 + 1\text{-}C_4H_9$
$H + C_4H_{10} \rightarrow H_2 + 2\text{-}C_4H_9$
$H + C_2H_4 \rightarrow H_2 + C_2H_3$
$H + C_3H_6 \rightarrow H_2 + C_3H_5$
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$
$CH_3 + C_3H_8 \rightarrow CH_4 + n\text{-}C_3H_7$
$CH_3 + C_3H_8 \rightarrow CH_4 + iso\text{-}C_3H_7$
$CH_3 + C_4H_{10} \rightarrow CH_4 + 1\text{-}C_4H_9$
$CH_3 + C_4H_{10} \rightarrow CH_4 + 2\text{-}C_4H_9$
$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3$
$CH_3 + C_3H_6 \rightarrow CH_4 + C_3H_5$
$C_2H_5 + C_3H_8 \rightarrow C_2H_6 + n\text{-}C_3H_7$
$C_2H_5 + C_3H_8 \rightarrow C_2H_6 + iso\text{-}C_3H_7$
$C_2H_5 + C_4H_{10} \rightarrow C_2H_6 + 1\text{-}C_4H_9$
$C_2H_5 + C_4H_{10} \rightarrow C_2H_6 + 2\text{-}C_4H_9$
$n\text{-}C_3H_7 + C_2H_6 \rightarrow C_3H_8 + C_2H_5$
$iso\text{-}C_3H_7 + C_2H_6 \rightarrow C_3H_8 + C_2H_5$
$n\text{-}C_3H_7 + C_2H_4 \rightarrow C_3H_8 + C_2H_3$
$iso\text{-}C_3H_7 + C_2H_4 \rightarrow C_3H_8 + C_2H_3$