

## GAS PHASE PHOTOLYSIS OF ACETONE IN THE FAR ULTRA-VIOLET

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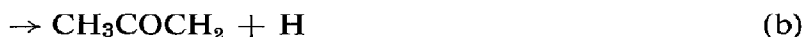
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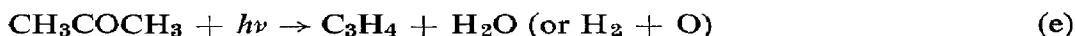
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### SUMMARY

The photolysis of acetone (pressure: 2 to 25 Torr,  $T$ : 300 K) was investigated at 147 nm (8.4 eV), 123.6 nm (10 eV) and 106.7–104.8 nm (11.6–11.8 eV). The quantum yields of the products  $H_2$ , CO,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_3H_8$ ,  $C_3H_6$ ,  $C_3H_4$ , and  $CH_3COC_2H_5$  were measured both in the presence and absence of free radical scavengers ( $C_2H_4$  or NO). These data, in conjunction with the results of deuterium-labelling experiments, demonstrated the occurrence of the following primary processes:



It is also suggested that the primary process:



occurs with a quantum yield of  $\sim 0.02$ . The quantum yield of "molecular" methane (process d) is 0.02 (147 nm), 0.028 (123.6 nm) and 0.043 (104.8–106.7 nm). The quantum of "molecular" hydrogen is 0.03 (147 nm) 0.26 (123.6 nm) and 0.28 (104.8–106.7 nm). The quantum yield of process (a) is  $0.7 \pm 0.1$  at 147 nm. At shorter wavelengths the quantum yield of the latter process could not be estimated because of the uncertain fate of the cations [ $\Phi(CH_3COCH_3^+) = 0.25$  at 123.6 nm and 0.21 at 104.8–106.7 nm] and the extensive dissociation of the internally excited species formed in the primary processes.

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## INTRODUCTION

The absorption spectrum<sup>1</sup> and the electron energy loss spectrum<sup>2</sup> of acetone vapor has been examined extensively. There are essentially three important valence transitions located in the regions about 4.5, 6.5 and 7.5 eV. From about 6.5 to 9.5 eV Rydberg series<sup>1f,3</sup> occur and above 9.7 lies the ionization continuum region. The vast majority of the photochemical studies<sup>4</sup> have been carried out in the weak first absorption band ( $\sim 4.5$  eV) which corresponds to a forbidden singlet  $n \rightarrow \pi^*$  transition. The C–C cleavage (process 1) is the predominant dissociative process occurring in this region.



However, at least at 313 nm (3.99 eV), process (1) occurs after intersystem crossing to the triplet state. There is an uncertainty as to the fraction of acetone molecules which dissociate from the first excited singlet state at the higher energy tail of the 4.5 eV absorption band.

A few photochemical studies have also been performed<sup>5</sup> in the much stronger absorption region around 6.5 eV which has been assigned to a  $n \rightarrow \sigma^*$  transition by several investigators. It would seem from the experimental studies by Howe and Noyes<sup>5b</sup> and by Potzinger and von Bunau<sup>5c</sup> that the acetone molecule excited to the  $\sigma^*$  state also dissociates nearly exclusively by cleavage of the C–C bond [ $\Phi(\text{CO}) = 1$ ]. Small quantities of  $\text{H}_2$  [ $\Phi(\text{H}_2) \sim 0.01$ ] were, however, reported<sup>5c</sup>. It is to be noted that decomposition of the acetone molecule excited to the singlet state in the 4.5 and 6.5 eV regions results in the formation of vibrationally excited  $\text{CH}_3\text{CO}$  radicals which do dissociate to yield CO and  $\text{CH}_3$ .

No photochemical studies have been carried out in the 7.5 eV region, and there is considerable uncertainty as to the transition involved<sup>2b</sup> there.

As far as the region beyond 7.5 eV is concerned, there is only one experimental investigation; namely, that by Leiga and Taylor<sup>6</sup> which deals with the photochemical decomposition of acetone at 147 nm (8.4 eV) and 123.6–116.5 nm (10–10.6 eV). In the latter study evidence was presented for the occurrence of primary processes which involve elimination of “molecular” hydrogen and methane. Quantum yields of these processes could not, however, be derived from the data. Also, because the percentage decomposition of the acetone was quite high (1.5 to 50%), reaction of intermediates with accumulated products complicated the interpretation of the observed product yields. The present study was undertaken with the expectation that reasonably accurate quantum yields could be obtained for the various products formed in the photolysis of acetone at 8.4, 10.0, and 11.6–11.8 eV at conversions not exceeding 0.2%. To obtain information concerning the primary dissociative processes, deuterium labelling and radical scavengers were used as diagnostic tools.

## EXPERIMENTAL

The microwave operated rare gas resonance light sources (Xe, Kr, Ar) used in this study have been described in a previous report from this laboratory<sup>7</sup>. The krypton resonance light source was provided with a CaF<sub>2</sub> window in order to eliminate the 116.5 nm line. The xenon resonance lamp (LiF window) emitted both the 147 nm line (98%) and the 129.5 nm line (3%). The radiation transmitted through a 0.32 cm thick LiF window attached to the argon resonance light source consisted of approximately equal intensities of the 104.8 and 106.7 nm lines. The incident light intensities were  $1-4 \times 10^{14}$ ,  $1-2 \times 10^{13}$  and  $2-5 \times 10^{13}$  quanta/s for the xenon, krypton and argon resonance lamps respectively. As noted before<sup>6</sup>, the transmission of the fluoride window diminishes from one experiment to the next. At the low conversions (0.01 to 0.04%) used in this study, the drop in transmission after one experiment was no more than 5%. Because the ionization potential of acetone is less than 10 eV<sup>8</sup>, the drop in transmission during radiation with the krypton (10.0 eV) and argon (11.6–11.8 eV) resonance light sources could be determined by monitoring the saturation ion current as a function of time.

The quantum yields of hydrogen, carbon monoxide and methane were based on the yield of <sup>13</sup>CO produced in the photolysis of <sup>13</sup>CO<sub>2</sub> [taking  $\Phi(^{13}\text{CO}) = 1$ ]<sup>9,10</sup>. The quantum yields of the other products were determined by using ethylene (1.5 Torr) as a chemical actinometer. The quantum yield of acetylene at 147 and 123.6 nm was established to be  $1 \pm 0.05$ <sup>10,11</sup>. At 104.8–106.7 nm,  $\Phi(\text{C}_2\text{H}_2)$  has been estimated to be  $0.75 \pm 0.05$ <sup>12</sup>. In the present study ethylene offers an advantage as an actinometer in that the acetylene product can be measured on the same gas chromatograph column as that used for analyzing the products formed in the photolysis of acetone. Actinometry experiments were performed after each acetone photolysis experiment.

Hydrocarbon products were analyzed by gas chromatography using a squalane column. Methyl ethyl ketone was measured using a diisodecylphthalate column. Hydrogen, carbon monoxide and methane were distilled at liquid or solid nitrogen temperatures and then analyzed by mass spectrometry. The isotopic composition of the acetylene, ethylene and ethane formed in the photolysis of CD<sub>3</sub>COCD<sub>3</sub>—CH<sub>3</sub>COCH<sub>3</sub> mixtures, was determined by trapping each of the hydrocarbon products at the exit of a gas chromatograph and introducing them into the ion source of a high resolution mass spectrometer. The acetone-d<sub>6</sub> used in the present study contained about 1% CD<sub>3</sub>COCD<sub>2</sub>H.

## RESULTS

All experiments were performed at ambient temperatures and at acetone pressures ranging from 2 to 25 Torr. Quantum yields obtained at a pressure of 5 Torr are reported in Table 1. Each value is based on three experiments whose con-

version is in a range where the quantum yields were found to be within experimental error invariant of percentage decomposition (0.01 to 0.04%). The accuracy of the quantum yields of 0.1 or higher is estimated to be 10%. The quantum yields of minor products such as  $C_2H_2$ ,  $C_3H_4$ ,  $C_3H_6$ , and  $C_3H_8$  are known only to within 20%. Within these limits of error no effect of pressure was observed on the yields of all products listed in Table 1, with the exception of methane and ethane. As anticipated from straightforward kinetic considerations<sup>4</sup>, a rise in pressure caused  $\Phi(CH_4)$  to increase and  $\Phi(C_2H_6)$  to decrease.

TABLE 1  
PHOTOLYSIS OF  $CH_3COCH_3$  QUANTUM YIELDS OF PRODUCTS

	Scavenger	H <sub>2</sub>	CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
147 nm	none	0.30	0.77	0.15	0.005	0.015	0.75	0.015	0.003	0.010
	NO	0.10	0.74	0.020	0.005	0.013	0.002	0.015	0.001	<0.002
123.6 nm	none	0.64	0.65	0.18	0.022	0.051	0.51	0.020	0.007	0.014
	NO	0.35	0.64	0.028	0.025	0.045	0.004	0.019	0.002	<0.002
104.8–106.7 nm	none	0.80	0.62	0.17	0.055	0.080	0.40	0.022	0.014	0.015
	NO	0.39	0.60	0.043	0.050	0.075	0.004	0.023	0.005	<0.002

Pressure: acetone, 5 Torr; NO, 0.1 Torr. Percentage decomposition: 0.01–0.04.

The  $C_3H_4$  product given in Table 1 consisted of allene ( $\sim 60\%$ ) and propyne ( $\sim 40\%$ ). Methyl ethyl ketone was a product whose quantum yield at an acetone pressure of 5 Torr was measured to be 0.044 (147 nm), 0.026 (123.6 nm) and 0.020 (104.8–106.7 nm). No methyl ethyl ketone was observed in the photolysis of acetone–NO mixtures. Biacetyl could not be detected as a product in the far ultraviolet photolysis of acetone [ $\Phi(\text{biacetyl}) < 10^{-4}$ ].

The isotopic analyses of the hydrogen, methane, ethylene and ethane are given in Tables 2–4. In addition, the isotopic acetylene formed in the 104.8–106.7

TABLE 2  
PHOTOLYSIS OF  $CH_3COCH_3$ – $CD_3COCD_3$  (1:1) MIXTURE QUANTUM YIELDS OF HYDROGEN AND METHANE

	Additive	H <sub>2</sub>	HD	D <sub>2</sub>	CH <sub>4</sub>	CH <sub>3</sub> D	CHD <sub>3</sub>	CD <sub>4</sub>
147 nm	none	0.10	0.076	0.027	0.056	0.017	0.057	0.041
	C <sub>2</sub> H <sub>4</sub>	0.042	0.024	0.014	0.022	0.004	0.012	0.011
	NO	0.043	0.026	0.015	0.009	0.001	0.001	0.005
123.6 nm	none	0.31	0.14	0.09	0.062	0.014	0.055	0.035
	NO	0.19	0.041	0.11	0.013	0.001	0.001	0.007
104.8–106.7 nm	none	0.44	0.19	0.13	0.075	0.013	0.057	0.032
	C <sub>2</sub> H <sub>4</sub>	0.22	0.041	0.09	0.040	0.010	0.026	0.011
	NO	0.22	0.052	0.12	0.014	0.001	0.002	0.010

Pressure of acetone: 23.4 Torr. Pressure of additive: 0.2 Torr.

TABLE 3

PHOTOLYSIS OF CH<sub>3</sub>COCH<sub>3</sub>-CD<sub>3</sub>COCD<sub>3</sub> (1:1) MIXTURE ISOTOPIC ANALYSIS OF ETHANE

	147.0 nm	123.6 nm	104.8-106.7 nm
C <sub>2</sub> H <sub>6</sub>	23.9	22.9	22.2
C <sub>2</sub> H <sub>5</sub> D	1.9	0.9	2.5
C <sub>2</sub> H <sub>4</sub> D <sub>2</sub>	0	0	1.5
C <sub>2</sub> H <sub>3</sub> D <sub>3</sub>	45.4	47.8	44.1
C <sub>2</sub> H <sub>2</sub> D <sub>4</sub>	3.3	3.0	4.0
C <sub>2</sub> HD <sub>5</sub>	1.8	1.9	2.5
C <sub>2</sub> D <sub>6</sub>	23.6	23.4	23.1
C <sub>2</sub> H <sub>3</sub> D <sub>3</sub> /(C <sub>2</sub> H <sub>6</sub> × C <sub>2</sub> D <sub>6</sub> ) <sup>1/2</sup>	1.91	2.07	1.94

TABLE 4

PHOTOLYSIS OF CH<sub>3</sub>COCH<sub>3</sub>-CD<sub>3</sub>COCD<sub>3</sub> (1:1) MIXTURE ISOTOPIC ANALYSIS OF ETHYLENE

	Scavenger	Percentage distribution				
		C <sub>2</sub> D <sub>4</sub>	C <sub>2</sub> HD <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> D	C <sub>2</sub> H <sub>4</sub>
147 nm	none	31.9	1.6	8.6	2.7	55.1
123.6 nm	none	22.9	3.6	12.4	4.9	56.2
	NO	29.6	0.8	10.5	1.7	55.6
104.8-106.7 nm	none	21.7	6.8	15.8	5.7	49.7
	NO	25.5	0.9	17.0	2.0	54.7
	O <sub>2</sub>	24.3	0.6	15.2	2.1	57.7

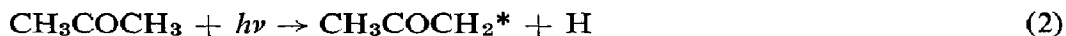
Pressure of acetone: 23.4 Torr. Pressure of additive: 0.2 Torr.

nm photolysis of a CH<sub>3</sub>COCH<sub>3</sub>-CD<sub>3</sub>COCD<sub>3</sub> (1:1) mixture at 10 Torr is as follows: C<sub>2</sub>H<sub>2</sub>, 58.1%; C<sub>2</sub>HD, 28.2%; and C<sub>2</sub>D<sub>2</sub>, 13.7%.

## DISCUSSION

*Photolysis at 147 nm (8.4 eV)*

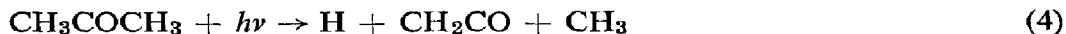
A cursory examination of the products given in Table 1 reveals that the photolysis of acetone in the Rydberg region distinguishes itself from that in the  $n \rightarrow \pi^*$  region in that (a) hydrogen is a major product and (b)  $\Phi(\text{CO})$  is less than unity even though no stable acetyl radicals are formed. These two facts, taken in conjunction with the observation that  $\Phi(\text{H}_2)$  is reduced when NO is added to acetone, point to the occurrence of the primary process:



probably followed by the unimolecular decomposition of the excited acetyl radical:



The energy requirement of the overall process:



is only 5.3 eV, which is well below the energy of the electronically excited acetone molecule. The overall process (4) can also be envisioned as the primary process (1) followed by decomposition of the  $\text{CH}_3\text{CO}$  radical into ketene and an H atom. This sequence of events is, however, improbable in view of the weak C–C bond in the acetyl radical<sup>13</sup>. The occurrence of process (2) is in accord with the contention of Potapov and Shigorin<sup>14</sup>, that a  $\pi$ – $\pi^*$  transition occurs between 7.7 and 8.5 eV which leads to cleavage of a C–H bond in acetone. The fact that HD is still a product when NO is added to a  $\text{CH}_3\text{COCH}_3$ – $\text{CD}_3\text{COCD}_3$  mixture (see Table 2) indicates that H atoms are formed with a substantial amount of kinetic energy. The isotopic analysis of the hydrogen observed in the free radical scavenged photolysis of an equimolar  $\text{CH}_3\text{COCH}_3$ – $\text{CD}_3\text{COCD}_3$  indicates, however, that a small amount of hydrogen is also formed by the unimolecular elimination of a hydrogen molecule. If one accepts that any bimolecular hydrogen formed in an acetone–NO or acetone– $\text{C}_2\text{H}_4$  experiment must be formed by a hot hydrogen atom abstraction reaction, and if one furthermore makes the simplifying assumption that hot atoms abstract equally fast from  $\text{CH}_3\text{COCH}_3$  or  $\text{CD}_3\text{COCD}_3$ , the “molecular” hydrogen contribution to the observed hydrogen can be taken as (Total hydrogen – 2HD). It follows that at 147 nm  $\Phi(\text{H}_2)$  molecular is equal to 0.03. As suggested by Leiga and Taylor<sup>6</sup>, the “molecular” hydrogen is most likely formed in the primary process:



The fate of the internally excited  $\text{CH}_3\text{COCH}$  radical formed in process (5) is not exactly known. It would seem, however, that a fraction of these species dissociate in the following manner:



The occurrence of this unimolecular reaction is evidenced by the fact that (a) ethylene is product in the photolysis of acetone (Table 1) and (b) the ethylene formed in the photolysis of an equimolar  $\text{CH}_3\text{COCH}_3$ – $\text{CD}_3\text{COCD}_3$  mixture consists mainly of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  (Table 4). Reaction (6) can be envisioned as an intramolecular insertion resulting in the formation of a highly excited cyclopropanone intermediate. An analogous mechanism has been proposed previously by Tchuikow-Roux and McNesby<sup>15</sup> in order to account for the formation of methylcyclopropane in the 147 nm photolysis of isobutane. The fact that  $\Phi(\text{C}_2\text{H}_4)$  is lower than the estimated yield of “molecular” hydrogen could be due to the formation of stable cyclopropanone or the isomerization to 3-propenal. No attempt was made to analyze for either of these products. Alternately,  $\text{C}_2\text{H}_4$  might be formed in a mechanism which involves elimination of  $\text{H}_2$  from the 1,3 position of acetone to form excited cyclopropanone as an intermediate.

All of the processes discussed above can account for only about 30–40% of the decomposition. An examination of the product yields formed in the presence and absence of radical scavenger (Table 1), and isotopic analysis of the ethane formed in the photolysis of a  $\text{CD}_3\text{COCD}_3$ – $\text{CH}_3\text{COCH}_3$  (1:1) mixture (Table 3)

shows that the ethane product is entirely formed by the recombination of methyl radicals. Furthermore, the methyl ethyl ketone product is most likely formed in the methyl radical reaction:



and the difference in the yield of methane observed in the absence and presence of NO (Table 1) may be attributed to methyl radicals. That is, the yield of methyl radicals formed in the photolysis of acetone at 8.4 eV is about 1.7. The occurrence of process (4) can account for not more than about 0.2–0.3 of this (if all the hydrogen originated in process 4). Therefore, we must write, as a major process in the photolysis of acetone at 8.4 eV:



The absence of biacetyl as a product shows that the excited acetyl radicals which might be formed as intermediates in process (8), dissociate under our experimental conditions ( $T = 300$  K,  $P = 5$  to 50 Torr). If we assume that most of the CO ( $\Phi \sim 0.7$ ) is formed in process (8), and the methyl radicals originate in process (8) [ $\Phi(\text{CH}_3) \sim 1.4$ ] and process (4) [ $\Phi(\text{CH}_3) \sim 0.2\text{--}0.3$ ] the total estimated quantum yield of methyl radicals  $\Phi(\text{CH}_3) \sim 1.7$  is in excellent agreement with the predicted values.

Besides processes (2), (5), and (8) there is substantial evidence for the occurrence of a primary process in which "molecular" methane is eliminated from acetone:



Methane is a substantial product in the free radical scavenger photolysis of acetone and furthermore, the methane formed in the photolysis of a  $\text{CH}_3\text{COCH}_3\text{--CD}_3\text{COCD}_3\text{--NO}$  mixture consists nearly exclusively of  $\text{CH}_4$  and  $\text{CD}_4$  (Table 2). The quantum yield of process (9) is estimated to be  $0.02 \pm 0.005$ . The elimination of  $\text{CH}_4$  from electronically excited acetone has recently also been suggested to occur at 313 nm (4 eV)<sup>4c</sup>. The evidence for such a process was based on plots of  $\Phi(\text{CH}_4)/\Phi(\text{C}_2\text{H}_6)$  versus acetone pressure which deviated from the anticipated behavior rather than on free radical scavenger experiments. Experiments carried out in our laboratory show that ( $\text{CH}_4$ ) molecular in the free radical scavenged photolysis of  $\text{CH}_3\text{COCH}_3$  at 313 nm ( $P = 5$  to 50 Torr) is  $< 10^{-4}$ .

So far, the  $\text{C}_3$  products ( $\text{C}_3\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_3\text{H}_8$ ) given in Table 1 have not been accounted for. Because the formation of  $\text{C}_3\text{H}_6$  and  $\text{C}_3\text{H}_8$  is largely inhibited by NO (Table 1), these products can logically be ascribed to the combination reactions:



The origin of the  $C_2H_3$  and  $C_2H_5$  radicals participating in these reactions is a matter of speculation. In contrast to the inhibiting effects of scavengers on the quantum yields of propane and propylene, the quantum yields of  $CH_2=C=CH_2$  and  $CH_3-C\equiv CH$  were found to be unaffected by the addition of  $O_2$  or  $NO$  (Table 1). A plausible primary process leading to the formation of  $C_3H_4$  products would be the elimination of  $H_2O$  from acetone:



This process, which has not been proposed before, requires only 1.7 or 3.0 eV depending whether  $C_3H_4$  is allene or propyne. It is also conceivable that the formation of  $C_3H_4$  involves the cleavage of the  $C=O$  bond in acetone followed by detachment of  $H_2$  from the internally excited  $C_3H_6$ . The overall process:



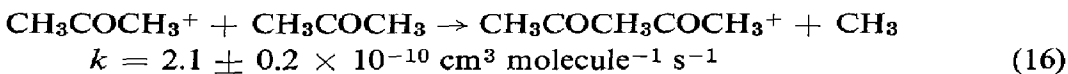
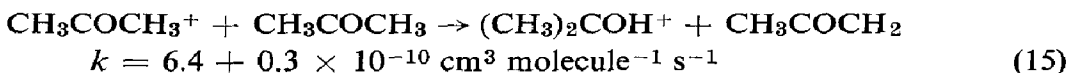
requires 6.8 to 8.2 eV depending on the structure of  $C_3H_4$ . The small yield of unscavengable propylene (Table 1) could be ascribed to stabilized propylene formed in a  $C=O$  cleavage process.

#### *Photolysis in the photoionization region*

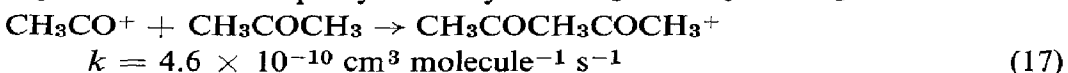
The energies corresponding to the 123.6 and 104.8–106.7 nm radiation (10.0 and 11.6–11.8 eV) are well in the photoionization region of acetone (ionizing potential = 9.7 eV)<sup>8</sup>. The photoionization quantum yield at 123.6 nm is 0.25 and reaches a value of around 0.21 in the 104.8–106.7 nm region<sup>17,18</sup>. At 123.6 nm only stable parent ions will be produced, while at 104.8–106.7 nm ( $P < 10^{-4}$  Torr) approximately 20% of the acetone cations dissociate<sup>19</sup> to yield  $CH_3CO^+$  (appearance potential = 10.2 eV)



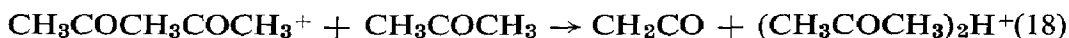
The parent ion is known to react very fast with acetone in the following manner<sup>19,20</sup>:



The  $CH_3CO^+$  ion reacts equally fast to yield  $CH_3COCH_3COCH_3^+$ :



The  $CH_3COCH_3COCH_3^+$  ion seems to react further with acetone to yield  $(CH_3COCH_3)_2H^+$ :





Subsequent collisions of  $(\text{CH}_3)_2\text{COH}^+$  or  $(\text{CH}_3\text{COCH}_3)_2\text{H}^+$  with acetone result in the formation of  $(\text{CH}_3\text{COCH}_3)_n\text{H}^+$  ions, where  $n = 4$  or higher<sup>20</sup>. We tentatively assume that the eventual neutralization of such a solvated ion occurs in the following manner:



Photolysis in the photoionization region results in a much higher quantum yield of  $\text{H}_2$  than that measured at 147 nm (Table 1). The isotopic analysis obtained from equimolar  $\text{CH}_3\text{COCH}_3\text{-CD}_3\text{COCD}_3$  mixtures (Table 2) as well as the quenching effect of NO (Table 1) points to the important role of H atoms in this wavelength region. There is, however, also a substantial increase in the yield of "molecular" hydrogen. From the data given in Table 2 the quantum yield of molecular hydrogen can be estimated at  $\sim 0.26 \pm 0.05$  at 10.0 eV and  $0.28 \pm 0.05$  at 11.6–11.8 eV. The "molecular" hydrogen can be ascribed to primary process (5). However, at these photon energies the overall process:



is energetically feasible. Such a process, which requires 8.24–8.74 eV, could occur *via* an excited  $\text{CH}_3$  radical formed in primary process (7) or *via* an excited  $\text{CH}_3\text{COCH}$  formed in primary process (5). The relatively sharp increase in  $\Phi(\text{C}_2\text{H}_4)$  at the higher photon energies (Table 1) seems to indicate, however, that the unimolecular reaction (6) remains an important mode of decomposition of the  $\text{CH}_3\text{COCH}$  radical and that the primary process (5) is an important contributor to the formation of "molecular" hydrogen. It is to be noted, however, that the increased contribution of  $\text{C}_2\text{H}_2\text{D}_2$  to the ethylene fraction produced in the high energy photolysis of  $\text{CH}_3\text{COCH}_3\text{-CD}_3\text{COCD}_3$  mixtures (Table 4) points to the occurrence of an unidentified bimolecular reaction yielding ethylene as a product. In contrast to the relatively sharp increase in the quantum yield of "molecular" hydrogen in going from the 147 nm to the 123.6–104.8 nm region, the quantum yield of "molecular" methane is seen to increase only slightly (see NO scavenged experiments in Tables 1 and 2).

As anticipated, in the photoionization region, the quantum yields of CO and of the  $\text{CH}_3$  radicals, as calculated from the yields of ethane, methane, and methyl ethyl ketone, are lower than at 147 nm. The ionic reactions discussed above probably do not result in the formation of CO, and less than one  $\text{CH}_3$  radical is expected to be formed per positive ion (reaction 16). The increased importance of "molecular" hydrogen will also have the net effect of lowering the estimated value of  $\Phi(\text{CH}_3)$ .

A detailed quantitative accounting of the primary processes contributing to the formation of the products observed in this high energy range is unwarranted. Many reactive intermediates including CH and  $\text{CH}_2$ , which have not been considered are probably produced. Also, although as indicated by the isotopic analysis of

the ethanes given in Table 3 of methyl radicals are clearly produced by cleavage of a C-C bond, there is no way to proportion the radicals among the various plausible decomposition processes. Finally, the modes of formation of several of the products remain unelucidated. An obvious example is the presence of acetylene as a significant product in the photoionization region. All that can be said on the basis of its isotopic analysis (see results) is that this particular product is formed in a bimolecular reaction.

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