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### Title

THE RADIOLYSIS OF BIACETYL VAPOR

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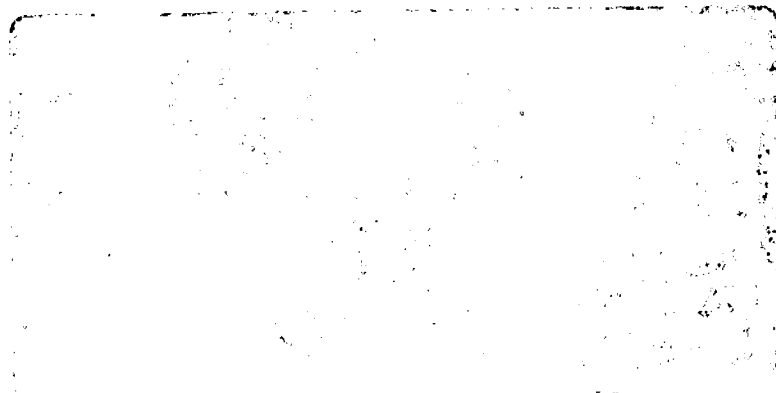
### Publication Date

1960-09-01

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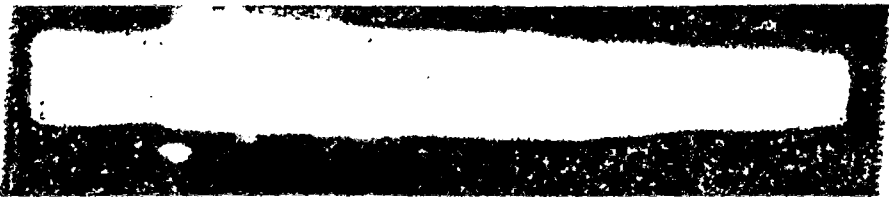
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UCRL-9363

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory  
Berkeley, California

Contract No. W-7405-eng-48

THE RADIOLYSIS OF BIACETYL VAPOR

Gilbert J. Mains and Amos S. Newton

September 1960

THE RADIOLYSIS OF BIACETYL VAPOR<sup>1</sup>Gilbert J. Mains<sup>2</sup> and Amos S. NewtonLawrence Radiation Laboratory  
University of California  
Berkeley, CaliforniaAbstract

The radiolysis of biacetyl vapor was studied at 25, 120, and 200° as a function of biacetyl pressure, using 4.5-Mev electrons from a microwave linear accelerator. At 25 and 120° the effect of dose rate was studied. At 25° the relative yields of H<sub>2</sub>, CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> were found to be independent of biacetyl pressure and dose rate. At 120° the relative yields of methane and ethane were found to be both pressure- and dose-rate-dependent. At 200° the relative yields of methane and ethane were found to be pressure-dependent. These observations are explained in terms of a free-radical mechanism involving free radicals with energies in excess of thermal energy.

THE RADIOLYSIS OF BIACETYL VAPOR<sup>1</sup>  
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Berkeley, California

September 1960

UCRL-9363

Introduction

Preliminary studies of the radiolysis of some simple ketone vapors have been reported<sup>3,4</sup> but extensive investigations of these systems have not been carried out. Ausloos has indicated that 85% of the methane produced in the radiolysis of liquid acetone could be explained in terms of a normal abstraction reaction by a methyl radical. The relative yield of methane to ethane found in the vapor phase radiolysis of acetone was far too large compared to the ratio found in the liquid phase radiolysis to be explained in terms of thermal radical reactions. A similar effect was found in the radiolysis of methyl ethyl ketone and diethyl ketone. Furthermore, the relative ratios of products normally attributed to abstraction reactions to those products normally attributed to radical combination reactions were much too high in the vapor phase to be accounted for in terms of thermal free radicals such as encountered in the photolysis of these compounds.<sup>5,6,7</sup> In view of the results of these experiments, a thermal radical mechanism would not seem to account for the product distribution obtained in the vapor-phase radiolysis of small aliphatic ketones.

In order to investigate this point further, the radiolysis of biacetyl vapor has been studied over the pressure range 5 to 30 mm Hg at 25, 120, and 200° by use of a pulsed electron beam current from a 4.5-Mev microwave linear accelerator. In two experiments the pulse rate was varied, and in two other experiments the current was varied. To determine dose-rate effects at 25° a few experiments were carried out with lower electron beam currents from a 2.0-Mev Van de Graaff accelerator.

### Experimental

Eastman Kodak White Label biacetyl was dried by allowing the liquid to stand overnight in contact with pre-ignited anhydrous sodium sulfate. After it was dried, the biacetyl monomer was distilled from the polymer and degassed by trap-to-trap distillation in vacuo. The biacetyl prepared in this manner was found to be free of impurities by both mass spectrographic and vapor chromatographic analysis. It was stored in an ampoule on the vacuum line at  $-80^{\circ}$  until used. Aside from the formation of traces of photolysis products, it was found possible to store solid biacetyl at  $-80^{\circ}$  for more than a month under these conditions without repurification.

The Pyrex bombardment cells were cylinders, 5.4 cm in diameter and 60 cm long. One end of the cell was a thin concave window through which the electron beam was directed; the other end was fitted with a glass break-seal to facilitate analysis. The clean dry cell was evacuated and flamed. When the cell was cool, the biacetyl vapor was admitted to the desired pressure as read on an oil multiplying manometer. The cell was isolated and a sample of the biacetyl vapor checked by mass spectrometric analysis for the absence of air, water, and other contaminants. After this check, the biacetyl in the bombardment cell was condensed in a cold finger at one end of the cell with liquid nitrogen and the cell was sealed off. In preliminary bombardments at room temperature the cells warmed to about  $35$  to  $40^{\circ}$  during the irradiation. In Van de Graaff experiments the cells were immersed in a water tank to reduce the temperature rise to less than  $1^{\circ}$ , and in microwave accelerator bombardments the cells were fitted with water jackets. If the bombardment was to be carried out at elevated temperatures the cell was inserted into a brass tube, 2.75 in. O.D. and 33.5 in. long, which was wrapped with three 300-watt heating tapes in parallel, then with asbestos tape and, finally, with glass wool matting. The power to the heaters was manually controlled by means of a variable transformer. The temperature of the system was determined by a thermocouple inserted near the middle of the brass oven. After some experience, the temperature of the cell could be controlled to  $\pm 1\%$  during bombardment.

After bombardment the cell was fitted with a stopcock and break-in device. The cell was then attached to the inlet of a Consolidated Electro-dynamics Corporation Model 21-103A Mass Spectrometer, the connecting line evacuated, the break seal ruptured, and the mass spectrum of the total gas

products determined. The cell was then removed to a vacuum line where the gaseous products were separated into three fractions, volatile at  $-160^{\circ}$ , volatile at  $-119^{\circ}$ , and volatile at  $-80^{\circ}$ . The PV of each fraction was measured and the mass spectrum of that fraction determined. The mass spectrum of the residual liquid was also run.

Most of the gaseous products were found to be in the  $-160^{\circ}$  fraction, which consisted of  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$ , CO, and  $C_2H_6$ . The  $-119^{\circ}$  fraction always constituted less than 10% of the total products (frequently less than 5%) and was found to contain mostly ketene (in the higher-temperature runs) and lesser amounts of  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_4$ ,  $C_3H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ . Because this fraction was so small it was analyzed only for the ketene. Since acetylene forms a complex with ketones and appears mainly in the incompletely analyzed  $-119^{\circ}$  fraction, the acetylene yields, although of the same order of magnitude as the ethylene yields, are not reported. The  $-80^{\circ}$  fraction consisted mainly of acetone and acetaldehyde in approximately equal amounts. The acetone was found to be incompletely removed from biacetyl at  $-80^{\circ}$ , and therefore the acetone yield was estimated from the mass 58 peak in the mass spectrum of the total gas. It is probable that acetaldehyde was also incompletely removed and the acetaldehyde yields reported should be regarded as minimal. A small peak in the mass spectrum of the total gas at mass 100 was assumed to be acetyl propionyl and a yield was estimated on this basis. Some very small peaks in the total gas spectrum at masses 101, 102, and 128 were not identified but probably arise from products of additions of H atoms, methyl radicals, or acetyl radicals to biacetyl during radiolysis.

The measurements of the beam currents in both the microwave linear accelerator and Van de Graaff irradiations were not reliable, owing to insensitivities of the metering systems used. Therefore, absolute yields per unit dose input have not been computed. An approximate number calculated from Expt. 85 showed a hydrogen yield of  $G = 0.6$ . As the hydrogen yield does not appear to be sensitive to environmental conditions, one may estimate G values for other products from this figure.

## Results and Discussion

### Experiments at Room Temperature

The results of twelve experiments at room temperature are given in Table I. Probably the most remarkable feature of these data is the dose rate,



TABLE I

## Radiolysis of Biacetyl Vapor at Room Temperature

ELECTRON SOURCE		MICROWAVE LINEAR ACCELERATOR								VAN de GRAAFF				
Variable Investigated		←Biacetyl Pressure→				←Total Dose→			←Geom.→	←Pressure and Dose Rate→				
Experiment No.		75A	75B	75C	75D	89A	89B	89C	85d	79A	79B	82C	84B	
Biacetyl Pressure (mm of Hg)		5	10	20	30	20	20	20	20	20	5	20	20	
Beam Current <sup>a</sup>		50ma	50ma	50ma	50ma	25ma	50ma	50ma	50ma	22.5µa	22.5µa	22.5µa	50µa	
Beam Time (seconds) <sup>a</sup>		0.81	0.81	0.81	0.81	0.18	0.36	1.08	0.81	1,800	1,800	1,800	810	
Temperature (°C)		25-35	25-35	25-35	25-35	22.5	22.5	22.5	25-40	25-50	25-50	25-26	25-26	
Product Yields (micromoles)		H <sub>2</sub>	4.8	7.2	15.6	19.4	1.8	7.1	19.8	11.7	6.6	1.7	7.3	4.8
		CH <sub>4</sub>	1.7	2.7	6.2	8.2	0.6	2.9	7.3	5.1	6.2	0.8	2.2	1.6
		C <sub>2</sub> H <sub>4</sub>	1.0	0.7	1.3	3.2	0.3	1.8	2.1	0.8	0.4	0.4	1.1	0.3
		C <sub>2</sub> H <sub>6</sub>	15.8	25.3	53.4	69.2	6.6	27.2	65.3	38.8	31.4	7.3	25.4	16.0
		CO	63.5	93.0	210.0	258.0	22.7	97.0	239.6	144.9	115.0	25.8	97.2	63.1
		CH <sub>3</sub> CHO <sup>b</sup>	-- <sup>e</sup>	--	--	--	--	3.7	5.0	16.5	--	1.6	4.5	3.7
		CH <sub>2</sub> CO	--	--	--	--	--	--	< .1	14.2	0.8	2.5	--	--
		(CH <sub>3</sub> ) <sub>2</sub> CO	10.2	17.4	35.8	47.4	8.0	13.0	50	--	18.3	5.3	28.7	21.6
CH <sub>3</sub> B <sup>c</sup>		1.6	2.7	5.8	--	2.8	4.8	8.7	--	2.2	0.9	3.1	2.6	
R <sub>CH<sub>4</sub></sub> (molecules/cc-sec)x10 <sup>-15</sup>		0.9	1.4	3.1	4.3	1.4	3.2	2.7	0.3	1.4x10 <sup>-3</sup>	1.7x10 <sup>-4</sup>	4.9x10 <sup>-4</sup>	8.0x10 <sup>-4</sup>	
R <sub>C<sub>2</sub>H<sub>6</sub></sub> (molecules/cc-sec)x10 <sup>-15</sup>		7.8	12.5	25.4	34.2	14.6	30.2	24.1	2.4	7.0x10 <sup>-3</sup>	1.6x10 <sup>-3</sup>	5.0x10 <sup>-3</sup>	7.9x10 <sup>-3</sup>	
R <sub>CH<sub>4</sub></sub> /R <sub>C<sub>2</sub>H<sub>6</sub></sub>		0.11	0.11	0.12	0.13	0.10	0.11	0.11	0.13	0.20	0.11	0.10	0.10	

a. Microwave accelerator yields pulsed beam which was operated at 30 pulses/sec for these experiments. The beam current in the 5-µsec square wave pulses was taken as the maximum current. The beam time was computed from the pulse rate, pulse duration, and total bombardment time.

b. Minimum yield. See text for explanation.

c. Acetyl propionyl abbreviation.

d. This bombardment was carried out in a 12-liter flask instead of the cylinders described in the text.

e. Not determined in this analysis.

pressure, and total dose independence of the relative yields of  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , and CO. The relative yields of these gases were essentially the same when the bombardment cell was a 12-liter flask. Furthermore, there cannot be a strong temperature dependence of the radiolysis products at  $25^\circ$ , because some of the first targets warmed up slightly during bombardment but did not show any marked effects of this temperature rise. The large yield of ketene in Expt. 85 is noteworthy and is possibly attributable to the ability of ketene to diffuse out of the reaction zone in the 12-liter cell and avoid further reaction. The beam filled the cylindrical cells after traversing a few inches and little "dead" volume was present in these cells. It is interesting that the yield of product gases in cells of various geometries was approximately as expected on the basis of the volume swept by the divergent electron beam.

#### Experiments at Elevated Temperatures

The results of ten experiments at approximately  $120^\circ$  and four experiments at  $200^\circ$  are given in Table II. The No. 78 series of experiments at about  $120^\circ$  and the experiments at  $200^\circ$  indicate that there is a pressure effect at both these temperatures. Although the relative composition of  $H_2$ ,  $C_2H_6$ , and CO remain approximately constant, the yield of methane increases approximately linearly with biacetyl pressure. The effect of raising the temperature is significant. The relative yield of methane at  $200^\circ$  is considerably larger than at  $120^\circ$ . Whereas the absolute yields of CO, acetone, ketene, and acetyl propionyl increase with increasing temperature, the yields of  $H_2$  and ethane do not show appreciable changes. Within our experimental errors, the yield of  $H_2$  depends only on the total energy input into the biacetyl and is independent of all other variables. The yield of ketene is much larger at  $200^\circ$  than at the lower temperatures, and at  $200^\circ$  increases with the square of the biacetyl pressure. The No. 88 series of experiments indicates an effect of total dose on the relative yields of products. Although the rate of methane production is constant, the rate of production of ethane decreases as the total dose increases. This would lead one to infer that a reaction product is competing for the ethane precursors. The effect of dose rate can be seen by comparing expts. 87A and 87B. The relative yield of ethane increased and the relative yield of methane decreased slightly at higher beam currents, but the relative yields of  $H_2$  and CO did not show significant changes. Finally, the effect of pulse rate is seen by comparing 86A and 86B.

TABLE II

## Radiolysis of Biacetyl Vapor at Elevated Temperatures

Variable Investigated	MICROWAVE LINEAR ACCELERATOR														
	←Biacetyl Pressure→			←Total Dose→			←Dose Rate→		←Pulse Rate→		←Biacetyl Pressure→				
Experiment No.	78B	78A	78C	88A	88B	88C	87A	87B	86A <sup>d</sup>	86B <sup>e</sup>	83A	83B	83C	83D	
Temperature (°C)	110-30	110-30	110-40	120±1	120±1	120±1	120±1	120±1	120±1	120±1	200±2	200±2	200±2	200±2	
Biacetyl Pressure (mm)	5	20	30	20	20	20	20	20	20	20	5	10	20	30	
Beam Current (ma) <sup>a</sup>	50	50	50	50	50	50	10	80	50	50	50	50	50	50	
Beam Time (sec) <sup>a</sup>	0.81	0.81	0.81	0.18	0.36	1.08	4.05	0.40	0.81	0.40	0.81	0.81	0.81	0.81	
Product Yield (micromoles)	H <sub>2</sub>	2.6	11.4	24.3	4.5	7.2	22.8	15.7	11.6	18.1	15.4	5.2	6.8	15.6	19.7
	CH <sub>4</sub>	5.9	42.6	113.0	9.1	17.4	59.3	43.4	29.0	37.6	52.4	28.7	62.1	167.7	278.1
	C <sub>2</sub> H <sub>4</sub>	0.5	1.2	3.2	0.4	1.1	2.7	0.5	2.4	2.9	1.6	1.9	3.4	5.9	7.5
	C <sub>2</sub> H <sub>6</sub>	10.4	46.3	93.1	20.6	32.7	91.5	54.5	52.6	73.6	64.8	17.3	25.0	45.7	79.0
	CO	52.8	223.0	489.0	74.9	124.7	369.2	261.5	203.2	281.4	277.4	103.8	192.7	428.2	705.9
	CH <sub>3</sub> CHO <sup>b</sup>	---	--	6.7	3.5	7.0	13.9	10.5	9.4	12.6	9.9	2.8	5.4	6.3	6.9
	CH <sub>2</sub> CO	--	11.1	39.8	--	0.6	--	--	--	--	10.0	--	11.6	55.7	131.0
	(CH <sub>3</sub> ) <sub>2</sub> CO	5	25	--	10	10	43	16	25	40	33	13	33	68	106
CH <sub>3</sub> BC <sup>c</sup>	4.5	9.8	--	6.6	8.8	14.0	4.4	11.0	1.2	14.4	4.9	11.5	18.5	22.7	
R <sub>CH<sub>4</sub></sub> (molecules/cc-sec)x10 <sup>-15</sup>	2.9	21.1	55.8	20.2	19.3	21.9	4.3	28.6	18.5	25.8	14.2	30.7	82.8	137.0	
R <sub>C<sub>2</sub>H<sub>6</sub></sub> (molecules/cc-sec)x10 <sup>-15</sup>	5.1	22.9	45.8	45.8	36.3	33.1	5.3	51.9	36.3	32.0	8.5	11.9	22.6	39.0	
R <sub>CH<sub>4</sub></sub> /R <sub>C<sub>2</sub>H<sub>6</sub></sub>	0.57	0.92	1.22	0.44	0.53	0.66	0.81	0.55	0.51	0.81	1.67	2.58	3.66	3.51	
R <sub>CH<sub>4</sub></sub> /R <sub>C<sub>2</sub>H<sub>6</sub></sub> (B) x10 <sup>10</sup>	2.5	2.2	2.7	1.5	1.6	1.8	0.9	1.9	1.5	2.2	9.5	8.7	8.5	7.1	

a. The beam current in the 5μsec square wave pulses was taken as the maximum current. The beam time was computed from the pulse rate, pulse duration, and total bombardment time. Unless otherwise noted the pulse rate was 30 pulses/sec.

b. Minimum yield. See the Text for explanation.

c. Acetyl proionyl.

d. Pulsed at 7.5 pulses/sec.

e. Pulsed at 60 pulses/sec.

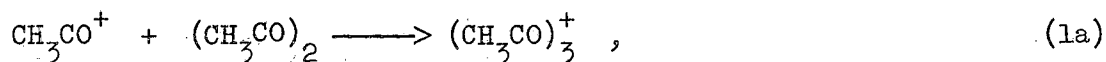
f. Not determined in this analysis.

The relative yield of methane was less when the accelerator was operated at 7.5 pulses/sec than at 60 pulses/sec. The relative yield of acetyl propionyl was also larger at the higher pulse rate, whereas the yields of other products were essentially independent of pulse rate.

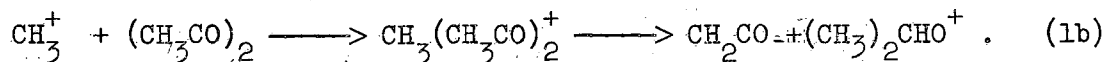
### Mechanism

It is apparent from the studies at 25° that the majority of the reaction products at 25° must arise by a mechanism which is essentially independent of dose rate, total dose, and biacetyl pressure, and which exhibits a small temperature coefficient. These conditions alone rule out the thermal radical mechanism proposed for the photolysis studies.<sup>8,9,10,11</sup> Furthermore, a thermal radical mechanism can be ruled out on the basis of the relative methane/ethane yields. Using Ausloos and Steacie's ratio of specific rate constants, i.e.,  $R_{\text{CH}_4} / (R_{\text{C}_2\text{H}_6})^{1/2} = 0.65 \times 10^{-13} \text{ cc}^{1/2} \text{ molecule}^{-1/2} \text{ sec}^{-1/2}$ , we calculate that thermal radical abstraction could account for less than 0.02% of the methane found in expt. 89C.

Mechanisms that would fulfill the stringent requirements noted above could possibly be formulated based upon ionic intermediates, "hot" radicals, or excited-molecule reactions. Only two peaks in the mass spectrum of biacetyl appear from pressure dependence to have an ion-molecule reaction origin. One is at mass 129 and presumably arises from the reaction



whereas the other is at mass 59 and could arise by the reaction



It is difficult to see how these ion-molecule reactions can give rise to all the products observed in the radiolysis of biacetyl. Reaction (1b) could result in ketene and acetone as products, and the product ions,  $(\text{CH}_3\text{CO})_3^+$  and  $\text{CH}_3(\text{CH}_3\text{CO})_2^+$ , could serve as precursors for some of the radiolysis products. Similarly, excited-molecule reactions such as

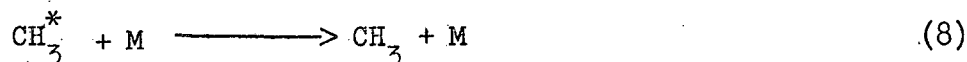
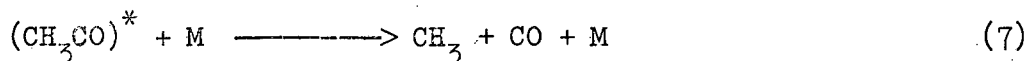
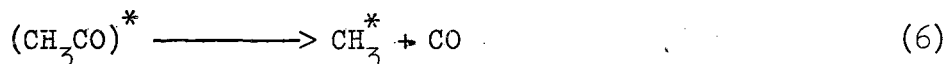
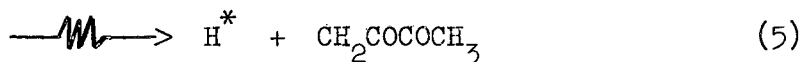
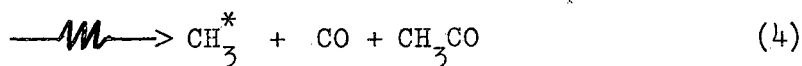
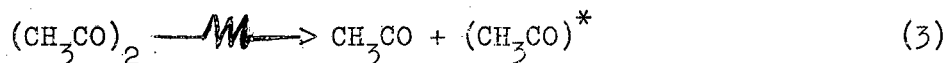


can possibly occur from high electronic (or vibrational) states of biacetyl.

Little is known of reactions such as Reaction (2). It is difficult to formulate a reaction scheme based upon excited-molecule reactions that accounts for the diverse radiolysis products. However, this does not preclude the possible formation of part of the radiolysis products by such a mechanism. Indeed, very small peaks in the mass spectrum of the product gases tentatively identified as arising from methyl ethynyl ketone, diacetylene, and butadiene may be attributed to products that arise from the decomposition of highly excited states of molecules or ions.

The striking similarity of radiolysis, pyrolysis, and photolysis products points to a common type of reaction. Since free-radical reactions have been invoked to account for photolysis and pyrolysis experiments it seems reasonable to modify these mechanisms to account, if possible, for radiolysis experiments. The modified mechanism must properly account for the high yields of methane and for the temperature and pressure dependencies observed in Tables I and II. A mechanism such as the following is one of several possible alternatives to explain the observations. In the reactions an asterisk (\*) denotes a radical or atom with energy in great excess of thermal energy. Unmarked atoms and radicals may be thermal or epithermal, as noted subsequently. We here define an epithermal radical as one having an energy in the broad range between thermal (in equilibrium with the surroundings) and "hot" (having sufficient energy to undergo reaction at essentially every collision).

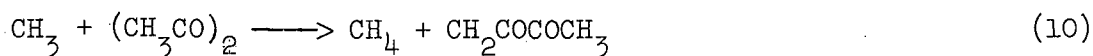
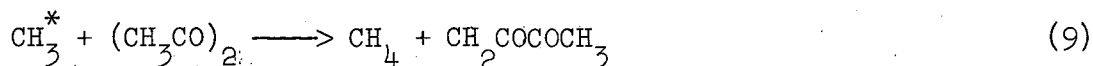
Radical and Atom Formation



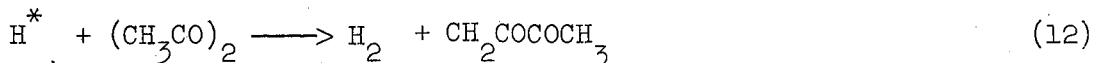
Reactions (3), (4), and (5) should not be regarded as elementary kinetic steps, since the formation of these "hot" intermediates may arise from the neutralization of ionic intermediates. In the above sequence the symbol M refers to any third body capable of removing all or part of the excitation energy. The thermalization of these "hot" radical intermediates will not occur in a single collision but in many collisions which will contribute to the formation of a distribution of epithermal radicals in the system.

Product Formation

Methane



Hydrogen



Ethane

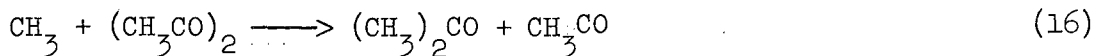


Carbon Monoxide

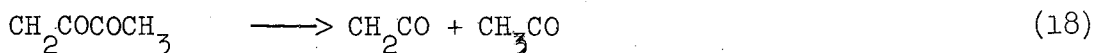
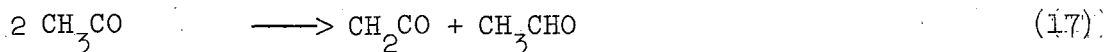


Also formed in Reactions (4), (6), and (7),

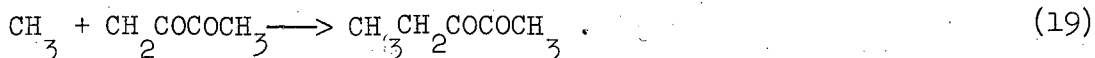
Acetone



Ketene and Acetaldehyde



Acetyl Propionyl



With the exception of the "hot" reactions, all of the above mechanistic steps have been proposed in photolysis studies.

At 25<sup>o</sup>, Reaction (9) must account for most of the methane. If Reaction (11) were to contribute appreciably to methane formation it would also be necessary to postulate identical pressure, dose, and dose-rate dependencies for the methyl and acetyl radical, and this seems unreasonable. The ketene observed in Expt. 85, Table I, apparently arises by Reactions (17) and (18) as well as by Reaction (11). As noted previously, this ketene may be consumed in the cylindrical cells where diffusion from the reaction zone is not possible.

At elevated temperatures the source of the methane must shift from Reactions (9) and (11) to Reaction (10) in order to explain the pressure dependence observed in the No. 78 and No. 83 series of experiments in Table II. It is to be noted that if one calculates the rate of Reaction (10), assuming only thermal radicals to contribute, then the rate is far too small to account for the methane at 200<sup>o</sup>. Therefore one must conclude that there is a large number of methyl radicals that have excess energy but are not energetic enough for Reaction (9) to occur appreciably at room temperature. Increasing the temperature provides the activation energy necessary for these epithermal radicals to react. It is not possible to estimate any expected value for the reaction rates of these epithermal methyl radicals because the shape of the energy-distribution curve is not known. It is not obvious whether such radicals are merely translationally "warm" or whether they also possess vibrational energy.

In Expts. 87A and 87B, the effect of dose rate at 120<sup>o</sup> was studied. At the higher dose rate, a relative increase in ethane compared with H<sub>2</sub>, CO and CH<sub>4</sub> may be attributed to the effect of radical concentration. The result obtained at the lower pulse rate, Expt. 86A, is essentially the same as for the other 120<sup>o</sup> experiments. The reason for the increase in methane at the higher pulse rate (Expt. 86B, Table II) is not obvious. Possibly the biacetyl vapor was not maintained at 120<sup>o</sup> at this high rate of energy input.

It is clear that the radiolysis of biacetyl can be explained qualitatively in terms of a free-radical mechanism similar to the photolysis mechanism, provided one postulates that some of the reactions occur while the methyl radicals are very energetic ("hot") and some of the reactions occur while some of the methyl radicals are merely epithermal. Since the relatively large yields of abstraction-type products has also been observed in acetone, methyl ethyl

ketone, and diethyl ketone radiolysis in the vapor phase, it appears that "hot" and epithermal radical reactions are common in the radiolysis of ketone vapors. The effect of passing from the vapor phase into the liquid phase can be explained in terms of the expected rapid thermalization of epithermal radicals in the liquid phase. Since little is known of the reactions of epithermal free radicals, further speculation regarding the biacetyl system seems unwarranted. Further experimental studies will be necessary to ascertain the details of such reactions.

#### Acknowledgments

The authors are grateful to Mr. Aldo F. Sciamanna for making the mass spectrometer runs and for aiding in the mass spectral analysis, and to Mr. William Everett for aiding in the electron irradiations with the microwave linear accelerator. The authors also wish to thank Dr. K. L. Hall and Mr. Norman Shields of the California Research Corporation for use of their Van de Graaff accelerator and for aid in the irradiations with it,

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