

UNIVERSITY OF
CALIFORNIA

Ernest O. Lawrence

*Radiation
Laboratory*

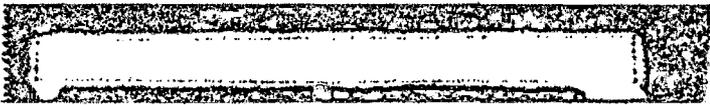
TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.



UCRL-9363-Rev.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

THE RADIOLYSIS OF BIACETYL VAPOR

Gilbert J. Mains, Amos S. Newton, and Aldo F. Sciamanna

March 14, 1961

ABSTRACT

The radiolysis of biacetyl vapor was studied at 25, 120 and 200° with pulsed electrons from a 4.2 Mev microwave linear accelerator. Effects of pressure, pulse rate and total dose were studied. At room temperature the relative yields of methane and ethane were only slightly dependent on experimental parameters, but at higher pressures the relative yields were pressure dependent. A free radical mechanism has been proposed to explain the formation of the major products and this is shown to qualitatively account for the experimental observations.

THE RADIOLYSIS OF BIACETYL VAPOR¹Gilbert J. Mains, Amos S. Newton,² and Aldo F. SciamannaLawrence Radiation Laboratory
University of California
Berkeley, California

September 1960

Introduction

Preliminary studies of the radiolysis of some simple ketones as liquids and vapors have been reported^{3,4,5} but extensive investigations of these systems have not been carried out. Ausloos and Paulson³ have 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 appears to be too large compared to the ratio found in the photolysis of acetone^{6,7,8,9} to be explained completely in terms of thermal radical reactions. A similar effect was found in the radiolysis of methyl ethyl ketone and diethyl ketone.³ In view of the results cited, a thermal radical mechanism by itself might be insufficient 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 4.2-Mev microwave linear accelerator. In several experiments the pulse rate was varied, and in two experiments the current was varied. To determine microscopic dose-rate effects at 25° a few experiments were carried out with lower electron beam currents from a 2-Mev Van de Graaff accelerator. Iodine scavenging experiments have also been run at each of these temperatures.

Experimental

Eastman Kodak White Label biacetyl was purified by a method similar to that of Groh.¹⁰ It was dried by allowing the liquid to stand overnight under vacuum and in contact with pre-ignited anhydrous sodium sulfate. After it was dried, the biacetyl monomer was vacuum distilled from the polymer and degassed by trap-to-trap distillation in vacuo. It was finally distilled onto another sample^{of} pre-ignited anhydrous sodium sulfate in the storage bulb to stand overnight. 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° until used. Aside from the formation of possible traces of photolysis products, it was found possible to store solid biacetyl at -80° 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 liquid nitrogen cooled finger at one end of the cell and the cell was sealed off.

Irradiations were made using a microwave linear electron accelerator (Linac) at the Lawrence Radiation Laboratory. This produces a pulsed beam of electrons with a pulse length of 5 microseconds and a pulse current variable

from 10 to 100 milliamperes. The pulse repetition rate is variable. Most irradiations were made at 50 ma/pulse and 30 pulses per second. The electrons have a mean energy of about 4.2 Mev and hence traverse the entire target cell in gas phase work. Because of scattering in the windows, the entire cell, except for a small region at the front, was covered by the beam, though variations in intensity undoubtedly occurred along the length of the cell. During this work it was found that the reproducibility of individual pulses from this accelerator was probably not better than $\pm 20\%$, and variations in dose and dose rate were occurring within these limits. A regulating circuit was later added to the injector and deviations were reduced to about $\pm 5\%$. Most of the work reported here was done without the additional regulation. The Van de Graaff accelerator used was a 2 Mev High Voltage Engineering Company machine at the California Research Corporation. Owing to insensitivity of the current metering systems in both the Linac and Van de Graaff installations, measurement of the integrated beam current at the levels of operation used were only approximate.

In early bombardments at room temperature the cells, cooled only with an air blast, warmed to about 35° 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° , and in later microwave accelerator bombardments the cells were fitted with water jackets and the water temperature controlled to 25° . If the bombardment was to be carried out at elevated temperatures the cell was inserted into a thick wall brass tube, ^{70 mm} 270 mm i. O. D. and ^{85 cm} 385 cm long. This was wrapped with three 300 watt heating tapes connected 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. The temperature variation along the length of the oven was less than 2° at 200° . After some experience, the temperature of the cell could be controlled to $\pm 2^{\circ}$ during bombardment.

In experiments where I_2 was added, the cell was equilibrated at 25° with I_2 vapor, this was then frozen out in a side-arm tube connected with a stopcock, the biacetyl added to the desired pressure, frozen out and the I_2 added from the sidearm. If more than 0.31 mm I_2 pressure were added, it was achieved by making multiple equilibrations of the cell and respectively freezing each in the sidearm. Blank experiments in which the I_2 was titrated with sodium arsenite indicated that the system used achieved 88% saturation of I_2 at 25° in the two minute time allowed for equilibration. Blank experiments also showed the thermal reaction between iodine and biacetyl at 200° to be negligible in one hour of heating. Stopcocks through which I_2 was passed were greased with Fluorolube MG (Hooker Electrochemical Company). Some experiments at 25° were run with no stopcocks in the loading system. These gave the lowest CH_4 yields.

After bombardment the cell was fitted with a stopcock and break-in device. The cell was then attached to the inlet of a Consolidated Electrodynamics Corporation Model 21-103A Mass Spectrometer, the connecting line evacuated, the break seal ruptured, and the mass spectrum of the total gas determined. The cell was then removed to a vacuum line where the gaseous products were separated into three fractions, volatile at -160° , volatile at -119° , and volatile at -80° . The FV of each fraction was measured and the mass spectrum of that fraction determined. The mass spectrum of the residual liquid was also run. Not all samples were subjected to all these measurements, but in all cases at least a -160° fraction was analyzed.

Most of the gaseous products were found to be in the -160° fraction, which consisted of H_2 , C_2H_2 , C_2H_4 , CO , C_2H_6 and CO_2 . The -119° 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 , CO_2 , and possibly C_4H_{10} . Because this fraction was small it was analyzed only for the ketene and CO_2 . Since acetylene forms a complex with ketones and appears partly in the incompletely analyzed -119° fraction, the acetylene yields, although somewhat higher than the ethylene yields, are minimum yields. The -80° fraction consisted mainly of acetone and acetaldehyde in approximately equal amounts. The acetone was found to be incompletely removed from biacetyl at -80° , and therefore the acetone yield was estimated from the mass 58 peak in the mass spectrum of the total gas. It is possible 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 all due to acetyl propionyl and a yield was estimated on this basis. Some very small peaks in the total mass 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. Acetone, acetyl propionyl and acetic acid were identified by gas chromatography and mass spectrometry in the residual liquid.

Results and Discussion

Products and Yields.

Approximate yields of products, expressed as molecules of product per 100 ev. absorbed, have been calculated for the major radiolysis products and are listed in Table I. These values are normalized to a constant H₂ yield, as this product was found to be almost independent of variations in the radiation parameters. The dose calibration was done in a special target cell consisting of a 12 liter flask with a thin window blown in one side. The geometry of this cell was such that all electrons, except the few scattered at very wide angles, had approximately the same path length through the cell. Hence the energy absorbed was calculated from the mass of biacetyl in the path and the mass absorption coefficient of 4 Mev electrons. Such runs were limited to 25°. As some product yields are dependent on pulse rate, total dose, pressure, or pulse current, these G values should be used only as guides to the order of magnitude of yields under other conditions of irradiation.

A few other products are present in small yields and analyses for them were not feasible nor was the identification certain in all cases. These include methyl acetylene, diaacetylene, vinyl acetylene, butadiene, vinyl methyl ketone, acetic acid (yield at 25° about equal to that of acetyl propionyl), and at least two unidentified products boiling higher than acetyl propionyl.

Effects of Experimental Parameters at Room Temperature.

The effect of pressure, total dose, and pulse repetition rate, and the effect of a continuous beam as compared to a pulsed beam were studied

at 25°. Table II summarizes these data. The outstanding feature of these results is the small effect of these experimental parameters on the relative yields of the various products. Within experimental error the yield of C₂H₆/CO, H₂/CO and CO₂/CO are constant. The ratio of CH₄/C₂H₆ increases slightly with increasing pressure and with total dose. This latter ratio is lower in the Van de Graaff runs than in the Linac runs. On the other hand the ratio CH₄/C₂H₆ is higher in the 12 liter cell where dead space exists. This result is expected where diffusion of methyl radical into areas of low radical density is possible. The apparent agreement in $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ (B) (hereafter designated as Z) between the Linac and the Van de Graaff runs at the same pressure is probably fortuitous. If a different pulse rate on the Linac had been chosen, the agreement would not have been as good.

The effect of pulse rate gives a measure of radical lifetime in the system. If one considers the disappearance of methyl radicals to form ethane, then a single 5 u sec. pulse at 50 ma current will yield an initial methyl radical concentration of 0.7×10^{12} radicals per ml (assumed equal to the CO yield). Using the rate constant for methyl radical recombination of $10^{13.6}$ mole⁻¹ cc sec⁻¹, the calculated time to reduce the methyl radical concentration to half its initial value is 22 milliseconds. Because methyl radicals also disappear by reaction with other radicals, e.g. with acetyl, this probably represents a maximum value.

If $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ for each pulse rate (at constant pressure) is plotted against the time between pulses, and if each pulse is an individual event, then the points should follow a line proportional to $t^{-1/2}$. On the other hand, if the pulses are overlapping, there should be a deviation from this line. In Fig. 1, this has been plotted and it is apparent that the deviations

from the $t^{-1/2}$ law start at about 30 milliseconds between pulses. Therefore the mean radical life in this system must be less than 30 milliseconds. The agreement between the calculated value of 22 milliseconds and the curve is sufficient to conclude that the bulk of the methane and ethane must be formed by thermal radical reactions at room temperature. A small increase in the ratio $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}$ with time between pulses was observed even to times of one second between pulses. This observation might be interpreted as indicating the existence of a few very long lived methyl radicals in the system, these disappearing mainly by abstracting hydrogen from biacetyl.

Experiments at Elevated Temperatures.

The results of ten experiments at 120° and four experiments at 200° are shown in Table III. Although the ratio of H₂, CO, C₂H₆ and CO₂ do not change with pressure, the relative yield of methane increases with pressure at both 120 and 200°. At 200° the relative yield of ketene increases directly with pressure. Hydrogen and ethane show no temperature coefficient. The No. 88 series of experiments shows a small effect of total dose on the products. Whereas the rate of H₂/CO is constant, the ratios C₂H₆/CO decreases with total dose and the ratios CH₄/CO and CO₂/CO increase with dose. This would lead one to infer that a reaction product is competing for the ethane precursors. At the lower and higher beam currents in expts. 87A and 87B, the ratios of CH₄/CO and C₂H₆/CO definitely indicate more methane to result at 10 ma than at 80 ma. beam current.

Iodine Scavenger Experiments.

The results of adding I₂ vapor as a radical scavenger are shown in Table IV. These results have been converted to G values for comparison with Table I. The yield of CO at 25° was used as a basis for the conversion from the yield of product per unit time of irradiation to G values.

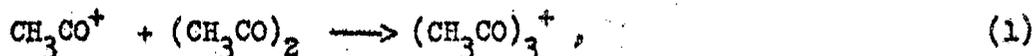
In all cases the yield of CH_3I is about equal to the yield of CO . While the CO does show a small temperature variation in the presence of I_2 , this is not much beyond the variations in CO yield at 25° , and is much less than found in the absence of iodine. It is also curious that in several cases the I_2 uptake was measured and while the variations were fairly large ($\pm 20\%$), at 25 and 120° the I_2 used is approximately equal to the CH_3I found. At 200° the I_2 uptake was about twice the CH_3I found, but the results at 120 and 200° are single experiments.

At room temperature, iodine reduces the yields of H_2 , CO , C_2H_2 , and CO_2 by about 25-30%. Methane is reduced by 85% and ethane by 99%. The methane result was however, extremely variable, and apparently trace impurities (unidentified) were able to greatly increase this figure. In one case a value of methane was found in the presence of I_2 which was 2.5 times as large as that found in the absence of I_2 . Such large variations in the yield of methane were not observed in the absence of I_2 , so the effect is probably specific for the presence of iodine. These observations cast a doubt on whether or not there would be any methane which would not be scavenged by I_2 in an ideal experiment.

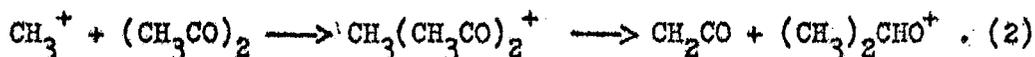
At high temperatures the amount of methane not scavenged by I_2 increases slightly, but the temperature coefficient is small compared to that observed in the absence of iodine. One can thus conclude that most of the methane and essentially all the ethane is produced by a precursor which is scavenged by I_2 . Presumably this precursor is the methyl radical. The results on iodine uptake indicate the acetyl radical either to be not scavenged (which we find difficult to believe), or the acetyl iodide undergoes a further reaction to regenerate iodine, either in the cell or in the titration of the excess iodine after separation.

Mechanism

It is apparent from the studies at 25° that most of the products must arise from a mechanism which is essentially independent of dose rate, total dose and biacetyl pressure. Iodine scavenging shows the precursors of ethane and most of the methane to be scavenged at all temperatures, and presumably these precursors are thermal methyl radicals. Ion molecule reactions for the production of methane do not appear likely as only two peaks in the mass spectrum of biacetyl appear (from pressure dependence measurements) to have an ion molecule origin. One is at mass 129 and presumably arises from the reaction:



whereas the other is at mass 59 and may arise from the reaction:



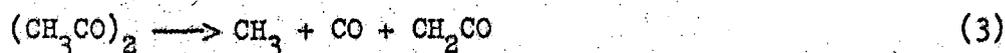
It is difficult to see how these ion molecule reactions can contribute to methane, though reaction (2) might contribute to ketene and acetone. Similarly excited molecule reactions might contribute but little is known about reactions of this type. However, products such as acetylene, diacetylene, methyl-vinyl ketone, and butadiene may arise from highly excited precursors. Except for hydrogen and a small fraction of the methane, the results are indicative of a thermal radical mechanism for the major products. Since such a mechanism has been suggested to account for photolysis and pyrolysis experiments¹²⁻¹⁷ it appears reasonable to modify these mechanisms to account for the radiolysis results. Stief and Ausloos¹⁸ have used thermal radical reactions in a proposed mechanism for the radiolysis of azomethane vapor. Such a mechanism must account for the following results. (1) The relative yields of radiolysis products are essentially dose, dose rate and pressure independent at 25°. (2) Iodine scavenger reduces methane by about 80%, H₂ by 20% and ethane by essentially 100%. (3) The rates of hydrogen and ethane

production are essentially independent of temperature while the methane shows a temperature coefficient which increases with temperatures.

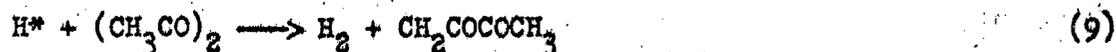
The failure to completely scavenge the hydrogen may be caused by hot radical reactions, molecular detachment, or failure of I_2 as an H atom scavenger. It is not easy to formulate reactions in which molecular detachment can occur to leave stable products. Therefore most of the hydrogen is postulated to occur by a hot radical mechanism and it is possible that a small part of the methane is also formed by a hot radical mechanism. Since ion neutralization might be expected to yield highly excited species, it is not unreasonable that such reactions occur.

The following sequence represents the mechanism suggested:

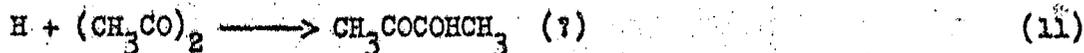
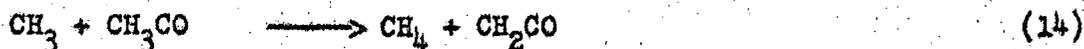
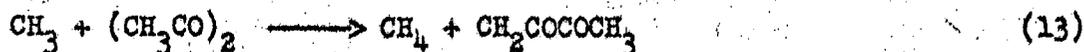
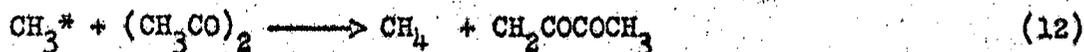
Radical Formation:



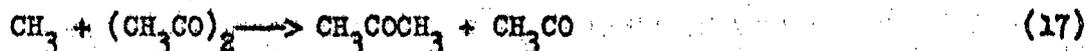
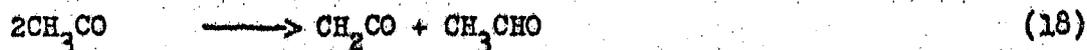
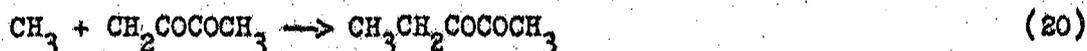
Reactions 3, 4, and 5 should not be regarded as elementary kinetic steps since the formation of these species may be the result of ion neutralization as well as direct energy absorption. There is no evidence of reaction (8) in this investigation and reaction (7) becomes of importance only at elevated temperatures. Sheats and Noyes¹⁴ have shown their photolysis data to be generally consistent with an initial fragmentation according to reaction (3) rather than fragmentation into two acetyl radicals.

Product FormationHydrogen

The bulk of the hydrogen must be formed by reaction (9) and its thermal analog or by a molecular process. Since the H atom concentration is low, the absence of a temperature coefficient for H₂ production is not necessarily an unequivocal criterion for the presence of hot H atoms. The direct combination of H atoms with a third body is probably of little importance as the yield of H₂ is independent of geometry and pressure. Furthermore, carbonyl compounds are known⁴ to be scavengers for thermal H atoms so they should have a very short lifetime in this system. The ultimate products of a reaction such as reaction (11) are not known.

MethaneEthaneCarbon Monoxide

Reactions (3), (6), and (7).

AcetoneKetene and AcetaldehydeAcetyl Propionyl

Except for the formation of H_2 and the hot methyl reaction (12), all of these reactions have been proposed in photolysis studies.

At 25° , reaction (14) must account for the bulk of the methane, with reaction (12) accounting for less than 20% of it and reaction (13) another 20% or so if one assumes Ausloos and Steacies' value of 0.65×10^{-13} for the function Z to represent the limiting value of the methane formed by abstraction by thermal radicals. These reactions thus account for the observation of a low activation energy near room temperature and for the relative independence of the methane/ethane ratio with pressure, dose rate, etc. The ratio of $\text{CH}_4/\text{C}_2\text{H}_6$ was significantly higher in the 12 liter flask where the radical could escape to a region of low radical concentration where reaction (13) would become significant. Reaction (14) has been shown to be of importance in the room temperature photolysis of biacetyl¹² and acetone⁶.

At elevated temperatures, reaction (13) is expected to become the major methane source. The evidence indicates it to do so. The activation energy for methane formation was an average of 4.7 k. cal. between 25 and 120° , and 7.0 k. cal. between 120 and 200° . This latter figure agrees with the photolysis results of Blacet and Bell,¹⁴ but is lower than those of Ausloos and Steacie. This, together

with the high values of the function Z at 120 and 200° compared to those of Ausloos and Steacie¹² and Sheats and Noyes¹⁵ indicate that under the high intensity conditions of our irradiations, reaction (14) may be a significant contributor to methane production even at 200°.

At all temperatures the material balance of $\text{CH}_4 + 2(\text{C}_2\text{H}_6)$ is about 55% of the CO yield. If acetone and acetyl propionyl are added, about 80% of the CO yield is accounted in terms of methyl radical utilization. The fate of the remaining 20% of methyl radicals is not known. The mechanism described does not account for the unsaturated hydrocarbons or for CO_2 . The latter compound does not appear to be a secondary product as its formation is approximately a linear function of total dose and pressure.

In experiments 87A and 87B, the effect of dose rate was compared and relatively more CH_4 was found at the low dose rate than at the higher dose rate. This is expected from the mechanism and the contribution of reaction (13) to methane formation at 120°.

The effect of temperature and pressure on the yields of acetone and ketene can be ascribed to the increased importance of reaction (17) to the production of acetone and reaction (19) to the production of ketene at elevated temperatures.

It is clear that the basic free radical mechanism which has been postulated to explain the photolysis of biacetyl, can also be used to qualitatively explain the major products in the radiolysis of biacetyl. Small contributions to methane at room temperature and most of the hydrogen production may be ascribed to "hot" radicals, though other mechanisms have not been completely eliminated. No mechanism has been proposed for the formation of unsaturated hydrocarbons and carbon dioxide, which products are not reported in the photolysis of biacetyl.

Acknowledgments

The authors wish to thank Mr. William Everette for aiding in the electron irradiations with the microwave linear accelerator, and to 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. The authors also wish to thank Dr. Peter Ausloos of the National Bureau of Standards for helpful suggestions and criticisms.

References

1. This work was performed under the auspices of the U. S. Atomic Energy Commission.
2. Author to whom requests for reprints are to be addressed.
3. P. Ausloos and J. F. Paulsen, *J. Amer. Chem. Soc.*, 80, 5117 (1958).
4. J. D. Strong and J. G. Burr, *Ibid* 81, 775 (1959).
5. J. C. McLennan and W. L. Patrick, *Can. J. Res.*, 5, 470 (1931).
6. P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, 33, 47 (1955).
7. W. A. Noyes, Jr., G. B. Porter, and J. E. Jolly, *Chem. Rev.*, 56, 49 (1956).
8. R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, 33, 1840 (1955).
9. P. Ausloos, *Can. J. Chem.*, 36, 400 (1958).
10. H. J. Groh, *J. Chem. Phys.*, 21, 674 (1953).
11. R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, 19, 85 (1951).
12. P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, 33, 39 (1955).
13. F. E. Blacet and W. E. Bell, *Disc. Faraday Soc.*, 14, 70 (1953).
14. G. F. Sheats and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, 77, 1421 (1955).
15. G. F. Sheats and W. A. Noyes, Jr., *Ibid* 77, 4532 (1955).
16. J. Heicklen and W. A. Noyes, Jr., *Ibid* 81, 3858 (1959).
17. E. W. R. Steacie, "Atomic and Free Radical Reactions", Reinhold Publishing Corp., New York, 1954, p. 354.

References (Con't)

17. E. W. R. Steacie, "Atomic and Free Radical Reactions", Reinhold Publishing Corp., New York, 1954, p. 354.
18. L. J. Stief and P. Ausloos, Paper presented at the 138th meeting of the Amer. Chem. Soc., New York, September, 1960.

Table I

Yields^{a)} of Products from the Irradiation of Biacetyl Vapor with Electrons

Product	G (product) at temperature specified		
	25°	120°	200°
H ₂ b)	0.55	0.55	0.55
CH ₄ c)	0.22	1.4	5.9
C ₂ H ₂	0.15	0.15	0.15
C ₂ H ₄	0.06	0.1	0.2
C ₂ H ₆	2.0	2.2	1.8
CO	7.4	9.2	16
C ₃ H ₆	0.03	---	---
C ₃ H ₈	0.06	---	---
CO ₂	0.1	0.4	0.6
CH ₂ CO ^{c,d)}	0.5	0.7	2.0
CH ₃ CHO	0.3	0.4	0.3
CH ₃ COCH ₃ ^{c)}	1:1	1.1	2.4
CH ₃ CH ₂ COCOCH ₃	0.3	0.5	0.7

a) Values listed are for irradiation with a pulsed beam, 5 μsec/pulse, 50 ma pulse current, 30 pulses/sec., 90 min. irradiation, and 20 mm biacetyl (measured at 25°), and cell geometry described in experimental section.

b) Values normalized on H₂ yield which is apparently dependent only on amount of radiation absorbed. Yields are probably accurate to ± 20%.

c) Value depends on radiation parameters.

d) Not found in all irradiations at 25° and 120°; behavior is erratic.

TABLE II

Radiolysis of Biacetyl Vapor at Room Temperature

ELECTRON SOURCE		← MICROWAVE LINEAR ACCELERATOR								VAN DE GRAAFF		
Variable		pressure				Total Dose			Geom. ^a			
Experiment No.		75A	75B	75C	75D	89A	89B	89C	89D	79B	82C	84B
Pressure (mm Hg) ^c		5	10	20	30	20	20	20	20	5	20	20
Beam Current (ma)		50	50	50	50	25	50	50	50	22.5 μ a ^b	22.5 ^b	50 ^b
Bomb Time (min)		90	90	90	90	20	40	120	90	30	30	13.5
Temperature		25-35	25-35	25-35	25-35	22.5	22.5	22.5	25-35	25-50	25	25
Product Yields (micromoles)	H ₂	4.77	7.23	15.62	19.50	1.80	7.09	19.75	11.72	1.68	7.29	4.77
	CH ₄	1.73	2.73	6.22	8.73	0.63	2.85	7.34	5.08	0.77	2.20	1.61
	C ₂ H ₂ ^d	--	--	--	--	0.41	1.49	3.64	1.92	0.26	0.24	0.49
	C ₂ H ₄	1.02	0.73	1.25	3.22	0.27	1.66	2.07	0.84	0.41	1.07	0.28
	C ₂ H ₆	15.8	25.3	53.4	69.2	6.59	27.21	65.35	38.77	7.32	22.4	15.96
	CO	63.5	93.0	209.7	258.5	22.7	97.0	239.6	144.7	25.8	97.2	63.1
	CO ₂	0.89	1.61	3.07	4.64	0.33	2.43	6.6	1.29	--	--	0.54
$R_{CH_4}/R_{C_2H_6}$		0.109	0.108	0.116	0.126	0.096	.105	0.112	0.131	0.105	.098	0.101
$R_{C_2H_6}/R_{CO}$		0.249	0.272	0.255	0.268	0.290	0.281	0.272	0.267	0.284	0.230	0.253
R_{H_2}/R_{CO}		0.075	0.078	0.074	0.075	0.079	0.073	0.082	0.081	0.065	.075	0.076
$[R_{CH_4}/R_{C_2H_6}]^{1/2}$ (B) $\times 10^{13}$		8.58	5.25	4.18	3.34	2.55	4.03	3.86	---	9.70	3.95	5.11

a) Irradiation cell was 12 liter spherical flask.

b) Continuous beam, beam current in μ amps.

c) Volume of cells = 1100 \pm 50 ml.

d) Minimum yield.

TABLE III

Radiolysis of Biacetyl Vapor at Elevated Temperature

Variable		← Pressure →			← Total Dose →			← Dose Rate →		← Pressure →			
Run No.		78B	78A	78C	88A	88B	88C	87A	87B	83A	83B	83C	83D
Temperature	110-130	110-130	110-130	110-130	120	120	120	120	120	200	200	200	200
Pressure (mm) ^a	5	5	20	30	20	20	20	20	20	5	10	20	30
Beam Current (ma)	50	50	50	50	50	50	50	10	80	50	50	50	50
Time Bombardment (min)	90	90	90	90	20	40	120	450	45	90	90	90	90
Product Yields (micromoles)	H ₂	2.62	11.4	24.3	4.48	7.16	22.8	15.7	11.6	5.17	6.82	15.64	19.76
	CH ₄	5.92	42.6	113.8	9.11	17.35	59.3	45.5	29.0	28.7	62.1	167.7	279.6
	C ₂ H ₂ ^b	0.5	1.4	4.6	0.8	1.5	4.3	--	2.3	1.1	1.7	3.3	9.8
	C ₂ H ₄	0.5	1.2	3.2	0.4	1.1	2.7	--	2.4	1.9	3.4	5.9	7.5
	C ₂ H ₆	10.4	46.3	93.1	20.6	32.7	89.7	53.8	52.6	17.25	24.1	45.7	79.4
	CO	52.8	223.	489.6	74.9	124.7	369.2	261.5	203.2	103.7	192.7	428.2	709.7
	CO ₂	-- ^c	7.9	23.5	2.5	4.6	17.0	6.6	8.9	4.4	7.2	12.8	22.6
	CH ₂ CHO	--	--	6.7	3.5	7.0	13.9	10.5	9.4	2.8	5.4	6.3	6.9
	CH ₂ CO	--	11.0	39.8	--	--	--	--	--	0.3	11.6	55.7	131.
	(CH ₃) ₂ CO	--	25	10	--	10	43	16	25	13	33	68	106
	CH ₃ CO ^d	--	9.8	6.6	--	8.8	14.0	4.4	11.0	4.9	11.5	18.5	22.7
	CH ₄ /C ₂ H ₆	0.57	0.92	1.22	0.44	0.53	0.66	0.85	0.55	1.66	2.57	3.67	3.52
	C ₂ H ₆ /CO	0.197	0.208	0.190	0.275	0.262	0.243	0.206	0.259	0.166	0.125	0.107	0.11
H ₂ /CO	0.051	0.051	0.050	0.060	0.057	0.062	0.060	0.057	0.059	0.035	0.036	0.02	
$[R_{CH_4}/R_{C_2H_6}^{1/2} (B)] \times 10^{12}$	3.6	3.1	3.9	2.10	2.24	2.67	1.36	2.77	13.5	12.4	12.2	10.3	

a) Pressure measured at 25°. Vol. cells 1100 ± 50 cc in each case.

b) Minimum yield.

c) Blanks refer to no determination of the product in these runs.

d) Acetyl propionyl.

TABLE IV

Yields of Products from the Irradiation of Biacetyl Vapor plus Iodine Vapor with Electrons.

Temperature	25° ^a	120°	200°
I ₂ pressure (mm)	0.3	0.9	0.9
Biacetyl pressure mm	20.0	20.0	20.0
Product ^c	G for product		
H ₂	0.38	.35	.49
CH ₄	.03 ^b	.07	.22
C ₂ H ₂	0.1	.09	.14
C ₂ H ₄	.03	0.02	.05
C ₂ H ₆	.02	.02	.01
CO	6.3	5.5	8.4
C ₃ H ₆	.013	--	--
C ₃ H ₈	.006	--	--
CO ₂	.07	.07	.16
CH ₃ I	5.9	5.2	17.7
I (atoms used)	6.4	5.3	14.8

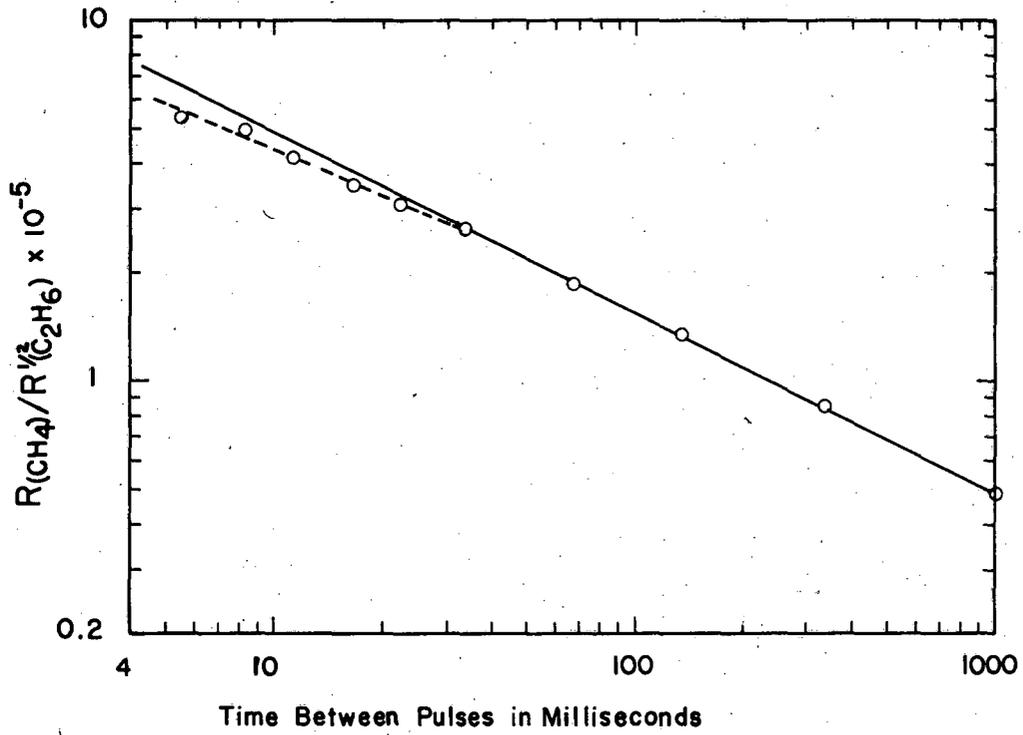
a) Represents average values from 7 experiments. Values at 120 and 200° are single experiments. 5 and 10 minute irradiations at 25°, 15 minute at 120 and 200°. Beam conditions 50 ma/pulse, 30 pulses/sec.

b) Result variable. Value listed represents lowest values found.

c) Acetone, ketene, acetaldehyde and acetyl propionyl were not studied.

FIGURE CAPTION

Fig. 1. Plot of $R_{\text{CH}_4} / R_{\text{C}_2\text{H}_6}^{1/2}$ vs. time between pulses for the irradiation of biacetyl vapor at 25° , 20 mm pressure, 50 ma pulse current, and selected repetition rates. Points at high repetition rates have been corrected for falloff in pulse current by normalization to a constant CO yield/pulse. Points at 16.7 and 33.3 m.secs. are averages of several close points. Solid line is of slope $t^{-1/2}$.



MU-22721

Fig. 1

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

