

TABLE VII. Calculated and observed CN frequencies for $N^{14}C^{13}AuC^{12}N^{14}$ and $N^{15}C^{12}AuC^{12}N^{14}$.

		Calculated for NCAuCN	Calculated for CNAuNC	Observed
$N^{14}C^{13}AuC^{12}N^{14}$	ν_1	2151.7	2151.9	2152.3
	ν_3	2100.8	2101.7	2101.6
$N^{15}C^{12}AuC^{12}N^{14}$	ν_1	2152.8	2152.6	2153.2
	ν_3	2116.7	2116.0	2117.9

from a combination of ν_1 or ν_3 with a lattice frequency of 32 or 51 cm^{-1} , respectively.

CN Frequencies of Monosubstituted Species

The force constants of Table IV were used to calculate the frequencies of the monosubstituted species. The

results are given in Table VII. Perhaps the most significant comparison is the difference of ν_3 for the C^{13} species and ν_3 for the N^{15} species. This is observed to be $16.3 \pm 0.3 \text{ cm}^{-1}$. From Table VII it is seen that the value calculated for NCAuCN is 15.9 while that calculated for CNAuNC is 14.3. Though this comparison is not conclusive, as anharmonicity was neglected, it stands as further confirmation of the structure NCAuCN as opposed to CNAuNC.

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Photochemical Studies in Flash Photolysis. I. Photolysis of Acetone*

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The high-intensity flash photolysis of acetone was investigated using an exploding wire as a light source. Experiments were conducted with the unfiltered light of the flash, containing light in the near as well as in the far ultraviolet region of the spectrum. The results show that the $\text{C}_2\text{H}_6/\text{CO}$ ratio in the reaction products is about 1.25 and is fairly insensitive to variation in acetone pressure. Addition of small amounts of biacetyl lowers the ratio still further. This is attributed to the deactivation of a long-lived excited acetone molecule formed in the ultraviolet region below 210 μ . Addition of butane lowers the ratio far below unity.

The CH_4/CO ratio has the constant value of 0.1 for various light intensities, acetone pressures, pressures of added butane or of carbon dioxide.

A convenient way of separating small amounts of ethane from very large amounts of carbon dioxide is described.

INTRODUCTION

THERE have been extensive investigations on the photolysis of acetone particularly by Noyes and co-workers and also by Steacie and his group.^{1,2} These studies have established that the main products of the photolysis are carbon monoxide, ethane, biacetyl, and methane. It has been shown³ that the major part of the photolysis reactions obeys a free radical mechanism. A study with high-intensity flash lamps has been

carried out by Norrish and co-workers,⁴ who conclude that their results are essentially in agreement with the low-intensity work.

In order to obtain more information about these free radical reactions, a high-intensity flash is used in the present work, whose intensity is about one million times greater than that used by the low-intensity workers. We therefore obtain instantaneously such a high concentration of free radicals that in our work radical-radical reactions should be favored over radical-molecule reactions. Such high-intensity work should give information particularly about the primary photochemical steps and indeed do we find evidence in our work to propose the existence of an excited state of acetone, formed by *far* ultraviolet light, which can be quenched by the biacetyl formed in the photolysis.

As the high-intensity light source, a thin Nichrome wire was used through which a bank of condensers

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¹ For reviews, see W. Davis, *Chem. Revs.* **40**, 201 (1947) and Noyes, Porter, and Jolley, *Chem. Revs.* **56**, 49 (1956).

² E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), second edition, Vol. I, Chap. V.

³ S. W. Benson and C. W. Falterman, *J. Chem. Phys.* **20**, 201 (1952).

⁴ Khan, Norrish, and Porter, *Proc. Roy. Soc. (London)* **A129**, 312 (1953).

was discharged. The wire explodes with the emission of ultraviolet light.⁵ The duration of the flash is about one-third of a millisecond.

EXPERIMENTAL

Materials

Acetone (Eastman Kodak White Label) was dried over anhydrous magnesium sulfate and was distilled under vacuum from -78°C to -195°C retaining the middle fraction. Biacetyl (Eastman Kodak White Label) was purified by distillation in an atmosphere of nitrogen. The middle fraction boiling at $87-88^{\circ}\text{C}$ was retained and dried over anhydrous magnesium sulfate. It was redistilled *in vacuo*, discarding first and last fractions, and was stored in the dark at dry ice temperature. *n*-butane (Matheson Instrument Grade) was purified by bubbling it through concentrated sulfuric acid and dried over sodium hydroxide and Drierite.

Apparatus

Carbon monoxide, ethane, and methane were the only decomposition products of the photolysis of acetone which were determined experimentally. The experiments were performed in a standard vacuum system. The photolysis part of the apparatus consisted of a two-stage diffusion pump, McLeod gauge, various storage vessels and a cylindrical reaction vessel having a volume of 158 cc and a diameter of 2.5 cm. This reaction cell was made of 20 cm of quartz tubing rounded at one end and attached to Pyrex by a graded seal. The Nichrome wire (BS gauge 40) to be exploded was arranged parallel to the reaction tube and after each flash the vessel was carefully wiped to remove any deposited metal. It was found convenient to wet the vessel with distilled water prior to the flash, since the tiny metal particles would float on that water film instead of adhering to the glass. The analysis part of the vacuum system consisted of a McLeod gauge and in succession, a one-stage diffusion pump, a Toepler pump, and a gas burette. Gas in the latter could be admitted to an oven containing cupric oxide which was used in the separation of carbon monoxide from methane. These latter two gases were removed from the acetone at -195°C and the ethane was pumped off subsequently at -160°C (the temperature of isopentane slush).

Some photolysis experiments were performed in the presence of small amounts of added biacetyl or large amounts of carbon dioxide or butane. The addition of carbon dioxide to the acetone required a modification in the separation of the ethane from the acetone-carbon dioxide mixture. In this case a U-trap filled with granules of calcium oxide (Fisher analytical reagent) was interposed between the trap containing

the mixture and the diffusion pump. The U-tube was kept at -78°C , while the trap containing the reaction mixture was maintained at -160°C . It should be mentioned that in the ethane-carbon dioxide separation it is necessary to keep the reaction mixture containing the carbon dioxide at a fairly low temperature, regardless of whether other gases such as acetone are present. This served to prevent the distillation of any appreciable amount of carbon dioxide into the calcium oxide tube where it would cover the granules with a thin layer of calcium carbonate, and so prevent further absorption of the carbon dioxide.

Since the over-all decomposition of acetone was usually of the order of 0.1% the actual amounts of the various decomposition products were quite small. In order to establish that our various separation methods were adequate, the appropriate artificial mixtures of the various gases were prepared and it was found that good separation was effected.

The flash apparatus has been described elsewhere.⁵ Experiments were carried out with the unfiltered light of the flash which contained wavelengths down to 200 $\text{m}\mu$ and below.

RESULTS

The results of the experiments are summarized below. For a given acetone pressure the carbon monoxide production is proportional to the intensity, as is seen in Fig. 1. For a given incident intensity, the carbon monoxide production as a function of acetone pressure is illustrated⁶ in Fig. 2.

The ethane to carbon monoxide ratio was observed to be insensitive to variation in the pressure of acetone. For example, the ratio was 1.24, 1.16, and 1.15 when the acetone pressure was 100, 50, and 25 mm, respectively. The value of the ratio in many experiments was on the average equal to 1.25. The ratio was observed to decrease with increasing number of flashes, or more precisely with increasing dosage of light. To ascertain

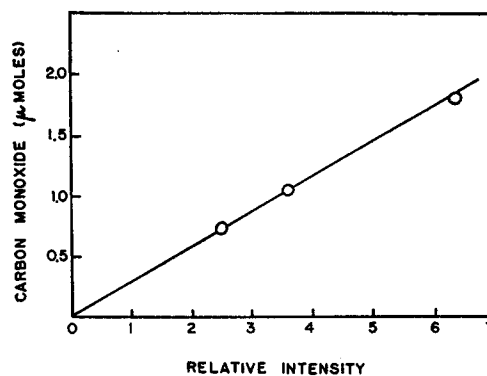


FIG. 1. Carbon monoxide production as a function of relative light intensity. The intensity was varied by changing the applied voltage, as discussed in reference 7. Pressure of acetone: 100 mm.

⁶ We are indebted to Mr. N. Slagowitz of this Laboratory for the data in Fig. 2.

⁵ G. K. Oster and R. A. Marcus, *J. Chem. Phys.* **27**, 188 (1957).

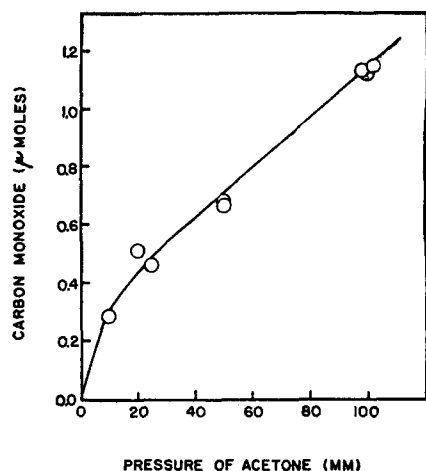


Fig. 2. Carbon monoxide production as a function of acetone pressure at constant incident light intensity.

whether this resulted from the formation of biacetyl during the photolysis, the effect of added biacetyl on the ratio was studied. When biacetyl, in amounts comparable to those actually formed during one flash, was added to the acetone prior to the flash, the ratio was found to decrease with increasing amounts of added biacetyl (Table I). A lowering of the ethane to carbon monoxide ratio to 0.95 has also been achieved by the addition of 400 mm of carbon dioxide to 100 mm of acetone. Large amounts of butane added to the acetone produced a drastic lowering of the ethane to carbon monoxide ratio to values far below unity (Table II).

It was further found that the methane to carbon monoxide ratio is equal to 0.1 and is seen from Fig. 3 to be independent of pressure and intensity. It was also essentially unaffected by the addition of carbon dioxide or butane. It appears from Table I to be slightly lowered by the addition of biacetyl, and this may be a result of an enhancement of carbon monoxide production rather than of a reduction of methane formation.

DISCUSSION

As is seen from Fig. 2, the carbon monoxide production is not directly proportional to the acetone pressure

TABLE I. Products of photolysis of acetone in the presence of biacetyl.^a

Pressure of acetone mm	Pressure of biacetyl mm	CO micro-moles	CH ₄ CO	C ₂ H ₆ CO	(CH ₃ CO) ₂ CO	CH ₃ COCH ₃ CO
100	...	1.14	0.10	1.24	0.24	
98	0.125	1.22	0.08	1.02	0.02	
100	0.400	1.20	0.07	0.86		
100	0.675	1.34	0.07	0.94		
...	43.0	3.25	0.02	0.33		0.35 ^b
...	0.4	0.02				
	+100mm Butane					

^a All experiments were performed with one flash of 8000 v at a wire distance of 1.95 cm from the center of the tube.

^b Estimated from material balance.

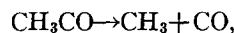
at constant incident intensity over the whole pressure range concerned. It follows that the same behavior applies to the absorbed intensity-acetone pressure relationship, since carbon monoxide is directly proportional to absorbed intensity (Fig. 1). The shape of the curve in Fig. 2 can be explained if it is assumed that absorption of light is appreciable in both absorption regions of acetone, namely in the near ultraviolet region with a maximum at 280 mμ and in the far ultraviolet with a maximum at 190 mμ. Since the molar extinction coefficient at that latter wavelength is 1000, absorption in the far ultraviolet region should be essentially one hundred percent except at very low acetone pressures where it falls off rapidly towards zero. In the near ultraviolet region, on the other hand, the absorbed intensity should be directly proportional to the pressure of acetone since the maximum molar extinction coefficient in that region is only 15. Indeed it has been found that this linear relationship is obeyed if acetone is photolyzed by the light of the flash with a Cellophane filter around the reaction vessel.⁷ Cellophane absorbs most of the light below 210 mμ.

TABLE II. Products of photolysis of acetone in the presence of *n*-butane.^a

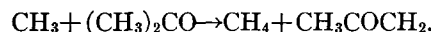
Pressure of acetone mm	Pressure of butane mm	CO micro-moles	CH ₄ CO	C ₂ H ₆ CO
50	200	1.92	0.12	0.45
50	50	1.96	0.11	0.82
90	10	2.82	0.11	1.17
10	10	0.75	0.11	0.64
10	90	0.52	0.12	0.41

^a All experiments were carried out with one flash of 8000 v at a wire distance of 2.25 cm from the center of the reaction tube and using a reflector.

In interpreting the results, it is first noted that several processes occurring at low intensities are definitely excluded at our high instantaneous radical concentrations. The excluded reactions are: the thermal decomposition of acetyl radicals,



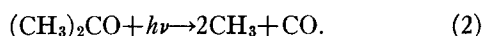
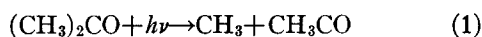
and the abstraction of a hydrogen atom from acetone by methyl radicals which are not "hot,"



Using known rate constants, these reactions can be shown to occur to an entirely negligible extent in comparison with the extent of radical-radical reactions. This is true notwithstanding the adiabatic temperature rise in the system (probably ~30°C. at most), which would tend to increase the occurrence of reactions with high activation energies. The temperature rise would increase these rates by less than a factor of 10, and it may be calculated that these reactions will still be negligible.

⁷ N. Slagowitz and R. A. Marcus (to be published).

The existence of an ethane to carbon monoxide ratio greater than unity indicates the presence of biacetyl among the reaction products and therefore the formation of acetyl radicals. Under the conditions of these experiments these radicals do not have time to decompose thermally to carbon monoxide, so that the latter can be assumed to arise from reaction (2).



Both primary steps are strongly supported by low-intensity studies.¹

The decrease of the ethane to carbon monoxide ratio with added biacetyl is not caused by some unexpected mode of decomposition of the added biacetyl by the light of the flash, as was proven by an experiment in which 43 mm of biacetyl alone were flashed (see

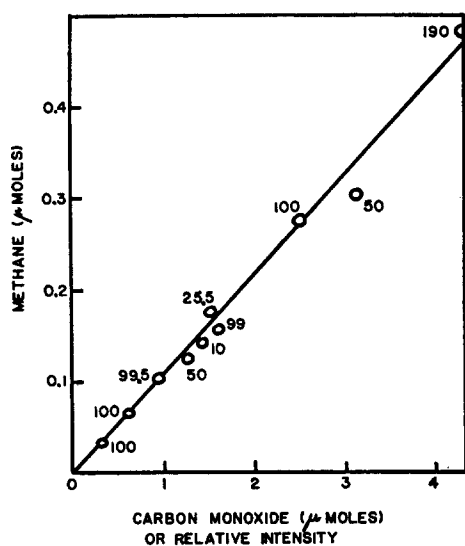


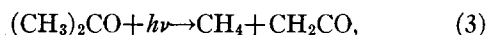
FIG. 3. Methane to carbon monoxide ratio dependence on intensity and acetone pressure. Numbers in graph denote acetone pressure in millimeters.

Table I). The results of that experiment were in exact agreement with those reported by Norrish and co-workers.⁴ In order to be certain that no abnormally high decomposition of biacetyl took place at our very low pressures of added biacetyl, 0.4 mm of biacetyl were flashed in the presence of butane (see Table I) which showed that the decomposition at that pressure was negligible compared with that of large amounts of acetone as in our experiments.

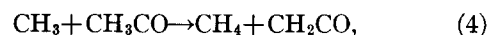
The lowering of the ethane to carbon monoxide ratio by biacetyl has not been observed with filtered light above 210 $m\mu$.⁷ It therefore appears that in the region below 210 $m\mu$ the primary step (2) occurs via an excited acetone molecule and that this molecule

can be deactivated by biacetyl. Its lifetime may be computed from the data in Table I to be of the order of 10^{-6} sec or longer if not every collision with biacetyl is effective in deactivation.

The independence of the methane to carbon monoxide ratio could be attributed to the intramolecular reaction,



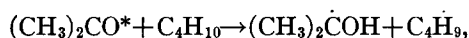
which would result in a proportionality of methane formation to intensity. Two alternative mechanisms for methane production are less tenable. One of these, reaction (4), does not account for the continued production,



of methane when acetyl radical formation is suppressed by added biacetyl or carbon dioxide. Another possibility for the formation of methane would be the reaction between "hot" methyl radicals and acetone although one would expect this reaction to be influenced by foreign gases. The experimental results, however, did not show any such dependence, except possibly a slight lowering of the methane to carbon monoxide ratio with added biacetyl.

The methane to carbon monoxide ratio was constant at about 0.1 even if the acetone were photolysed with Cellophane-filtered light where the wavelengths corresponding to the far ultraviolet absorption peak of acetone had been removed. This result eliminates at least for our experiments, the suggestion made by Norrish and co-workers,⁴ namely that methane is formed by the recombination of methyl radicals and hydrogen atoms, where the hydrogen atoms are formed by direct photolysis in the far ultraviolet region.

The lowering of the ethane to carbon monoxide ratio in the presence of butane to values far below unity (see Table II) is surprising and cannot be adequately explained at the present time. The use of artificial ethane, butane, and acetone mixtures definitely established that these small amounts of ethane could be separated quantitatively from the mixtures. (A number of cycles of freezing, pumping off of ethane and remelting were necessary.) Thus the phenomenon is quite real. It could possibly be caused by a reaction between excited molecules and butane:



followed by a recombination of these large radicals with methyl radicals (and with each other), thereby reducing amount of ethane formed.

Flash photolysis experiments are planned for the spectral region below 210 $m\mu$ with this exploding wire light source, but employing a sapphire or thin quartz reaction vessel.