The implications of such rapid NO₃-olefin reactions are significant to atmospheric chemistry. Using reactions 1-4 one can predict that in dry smog systems [NO₃] will be as much as 0.01% of the $[O_3]$ under conditions of high NO₂ concentrations.^{4,15} When this is combined with the large difference in the rate constants for O_3 and NO_3 it becomes apparent that olefin consumption by both species are roughly comparable. Conversely, reaction 3 contributes to the overall loss of NO_x in the later stages of smog reactions. This, in turn, will lead to a reduction in ozone levels, such that the conversion of NO_2 to NO_3 by ozone, with subsequent loss of the NO₃ from the O_3 -NO_x cycle, may control ozone formation in such systems.

Further studies of this and analogous reactions, as well as their implications in atmospheric chemistry, are in progress.

References and Notes

- (1) H. S. Johnston, J. Am. Chem. Soc., 73, 4542 (1951).
- E. D. Morris, Jr., C. H. Wu, and H. Niki, J. Phys. Chem., 77, 2507 (1973).
 P. A. Leighton, "Photochemistry of Air Pollution", Academic Press, New York, N.Y., 1961, p 188.
- (4) H. Niki, E. E. Daby, and B. Weinstock, Adv. Chem. Ser., No. 113, 14 (1972).
- E. D. Morris, Jr., and H. Niki, J. Phys. Chem., **78**, 1337 (1974).
 P. L. Hanst, J. Air Pollut. Control Assoc., **21**, 269 (1971).
 R. Louw, J. van Ham, and H. Niebohr, J. Air Pollut. Control Assoc., **23**,
- 716 (1973). (8) H. S. Johnston and R. Graham, Can. J. Chem., 52, 1415 (1974)

- (8) H. S. Johnston and R. Graham, Can. J. Chem., **52**, 1415 (1974).
 (9) S. M. Japar, C. H. Wu, and H. Niki, J. Phys. Chem., **78**, 2318 (1974).
 (10) E. D. Morris, Jr., and H. Niki, J. Phys. Chem., **75**, 3640 (1971).
 (11) E. D. Morris, Jr., and H. Niki, J. Phys. Chem., **77**, 1929 (1973).
 (12) G. Schott and N. Davidson, J. Am. Chem. Soc., **80**, 1841 (1958).
 (13) F. Cramarossa and H. S. Johnston, J. Chem. Phys., **43**, 727 (1965).
 (14) R. J. Cvetanovic, Adv. Photochem., **1**, 115 (1963).
 (15) K. L. Demerjian, J. A. Kerr, and J. G. Calvert, Adv. Environ. Sci. Technol. nol., 4, 1 (1974).
- (16) E. D. Morris, Jr., and H. Niki, J. Phys. Chem., 77, 1929 (1973).

Recent Work on the Photochemistry of Acetone in the Gaseous Phase^{1a}

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Publication costs assisted by the Robert A. Welch Foundation

A gas chromatographic method of determining biacetyl and 2-butanone during photolysis of acetone is described. Quantum yields of these two products have been determined as a function of pressure of acetone, of xenon, and of ethane as well as of temperature. The steps in the photolysis of acetone are briefly discussed. The primary yield at 265 nm is appreciably higher than at 313 nm. Further support for the wall formation of biacetyl is found.

I. Introduction

The photochemistry of acetone has been so extensively studied and reviewed that no attempt will be made to present a review at this time.²⁻⁴

The principal products of the photolysis of acetone vapor are CO, C₂H₅, CH₄, (COCH₃)₂, and CH₃CH₂COCH₃. At short wavelength H₂ is also formed.⁵ These products can be accounted for by the following steps:

$$CH_{2}COCH_{2} + h\nu = CH_{3} + COCH_{3}$$
(1)

$$COCH_2 = CO + CH_3$$
(2)

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$$
(3)

$$COCH_3 + COCH_3 = (COCH_3)_2$$
(4)

$$CH_3 + CH_2COCH_3 = CH_3CH_2COCH_3$$
(5)

$$CH_3 + COCH_3 = CH_3COCH_3 \tag{6}$$

(7)

$$CH_3 + CH_3 = C_2H_6$$

The present work gives better information than hitherto available on the steps which lead to the formation of biacetyl and of 2-butanone. A short discussion relates the implications of this work to conclusions previously drawn.

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II. Experimental⁶ Section

Acetone from Matheson Coleman and Bell was purified by gas chromatography on a 20% FFAP (free fatty acid Phthalate) Chromosorb P column 6 m in length and 1.0 cm in diameter at 100°. The acetone was shown by gas chromatography to be better than 99.92% pure.

Xenon, Union Carbide research grade, n-heptane, and ethane, both Phillips research grade, were used without further purification except for thorough degassing.

A grease free, mercury free vacuum system was used for all experiments. A cold cathode vacuum gauge showed the pressure upon prolonged evacuation to be less than $3 \times$ 10^{-7} Torr. The quartz photolysis cell was 20 cm long and 4.5 cm in diameter with a side window 6 cm from the front window, and 4.5 cm in diameter. The total volume including access tubing was 298 ml. The cell and connecting Teflon stopcock, Delmar with Viton O-ring, were housed in an electrically heated asbestos oven with front and rear Supracil windows.

The light source was a Hanovia 977B-1 1000 W mercuryxenon high-pressure lamp. The light was focused on the entrance slit of a Bausch and Lomb Model 33-86-45 monochromator with a reciprocal linear dispersion of 1.6 nm/ mm. Both the entrance and exit slits were 2 mm in width. A parallel beam about 2 cm² in cross section was passed centrally through the axis of the cell. The phototubes, RCA 935, and the photomultiplier tube, RCA 1P28, were arranged as described.⁶ Incident and transmitted intensities were measured every 5 min. The integrated intensity was measured by use of hydrogen iodide as an internal actinometer⁶ at 265.4 nm, and correction was made for 313 nm according to the manufacturer's characteristic curve of the RCA 935.

n-Heptane (0.15%) was added to the acetone to serve as an internal standard for product analysis by gas chromatography. It was shown to have no effect on the photochemistry of acetone under the conditions employed.

A microliter syringe was used to introduce the acetone. The acetone was then thoroughly degassed.

During photolysis of acetone reaction was about 0.2% or less complete. Carbon monoxide and methane were not determined and ethane was not measured quantitatively. The remainder of the mixture was condensed at -196° and analyzed on a Perkin-Elmer gas chromatograph with a 15.2 m column of *m*-bis(*m*-phenoxyphenoxy)benzene-apiezon L (MBMA) and a 15.2-m FFAP column in series at 40°. The products and the *n*-heptane were well resolved. A planimeter was used to measure peak areas.

Xenon (or ethane) was expanded into the cell onto the acetone from a Wallace-Tiernan pressure gauge. After photolysis the mixture was cooled to -120° and the xenon (or ethane) pumped off. The rest of the mixture was analyzed as before.

Photopolymerization of biacetyl formed during photolysis is believed to be unimportant under the present conditions because no polymer deposit was observed on the cell windows and there was no nonvolatile liquid residue remaining in the cell after evacuation.

III. Results

In reporting results on the photolysis of acetone it must be remembered that at room temperature both quantum yields of emission and of product formation are highly wavelength (as well as time) dependent.⁴ This means that these yields depend on the character of the so-called monochromatic light used and are not very reproducible from one laboratory to another. Generally speaking, this does not affect greatly the interpretation of results since trends are more important than absolute values.

As the temperature is raised variations with wavelength decrease and at 120° $\Phi_{CO} = 1.0$ within experimental error, thus making acetone at these temperatures suitable for use as an actinometer. The emission yield is so low as to make less than experimental error difference in the value of $\Phi_{CO} = 1.0$.

The integrated intensities of the light entering the cell were as follows: (a) 5.20×10^{14} photons sec⁻¹ at 265.4 nm; (b) 2.65×10^{15} photons sec⁻¹ at 313 nm. Fractions of radiation absorbed by the acetone were as follows at 26°:

Acetone pressure,

265.4 nm	313 nm
0.069	
0.131	
0.304	0.087
0,503	0.152
0.750	0.285
	265.4 nm 0.069 0.131 0.304 0.503 0.750

The results are summarized in Tables I-V.

TABLE I: Effect of Pressure on Biacetyl Yield at 26°a

	265.4	4 nm ()	1 hr)		
CH ₃ COCH ₃ pressure, Torr	2.5	5.1	12.7	25.5	51.0
Φ_{BiA}	0.35	0.34	0.33	0.28	0.26
	313.0) nm (2 hr)		
Φ_{BiA}			0.059	0.049	0.036

^a Absorption is so much weaker at 313.0 than at 265.4 nm that results at lower pressures would have little meaning. The longer time at 313.0 nm leads to a smaller conversion than at 265.4 nm.

TABLE II: Effect of Temperature on Yields of Biacetyl and of 2-Butanone during Acetone Photolysis^a

Tempera- ture, °C	26	36	45	55.5	64			
265.4 nm (1 hr)								
Φ_{BiA}	0.274	0.252	0.224	0.166				
Φ_{2-Bu}	0.007	0.013	0.018	0.023				
313.0 nm (2 hr)								
Φ_{BiA}	0.050	0.053	0.059	0.043	0.031			
Φ_{2-Bu}	0.002	0.005	0.007	0.010	0.021			
a Acotono nr	$\sim - 0$	5 5 Town						

^a Acetone pressure = 25.5 Torr.

TABLE III: Effect of Duration on Biacetyl Yields^a

		265.4	nm					
10	20	40	60	90	120	180		
0.274	0.276 me	0.274 an 0.27	$\begin{array}{c} 0.275 \\ 6 \pm 0.0 \end{array}$	0.278 01	0.276	0.276		
313 0 nm								
		010.0	60	120	180	240		
			0.049	0.050	0.044	0.042		
	me	an 0.04	6 ± 0.0	03				
	10 0.274	10 20 0.274 0.276 me me	265.4 10 20 40 0.274 0.276 0.274 mean 0.27 313.0 mean 0.04	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		

^a Temperature = 26°, acetone pressure = 25.5 Torr.

IV. Discussion

The new results concern mainly biacetyl and 2-butanone yields. The discussion will be based mainly on reactions 1 through 7.

Acetyl radicals undergo only reactions 2, 4, and 6. Since (6) re-forms acetone the net primary yield is the true primary yield less the yield of (6). Actually there is at present no unambiguous way to determine the difference between the actual primary yield and the true primary yield since scavengers run the risk of affecting the true primary yield.

It is generally agreed that (1) is the primary process at the wavelengths used.

If carbon monoxide is formed by a homogeneous firstorder reaction (2) and if biacetyl were formed by a homogeneous second-order reaction (4), one could write

$$\Phi_{\rm CO}^2/\Phi_{\rm BiA} = \rm constant \tag{8}$$

It is evident from the data in Table I and from earlier data⁷ that eq 8 is not obeyed during photolysis of acetone at 25° either at 313 or at 265 nm. It must be remembered that at constant incident intensity the number of photons absorbed per milliliter per second increases with pressure.

Other assumptions may be made in an attempt to explain the trends in product formation. If it is assumed that biacetyl is formed solely on the walls and that the rate of

265.4 nm (1 hr)		313.0 nm (2 hr)			
Xe pressure, Torr	Φ_{BIA}	Xe pressure, Torr	Φ_{BiA}		
0	0.275	0	0.050		
26	0.268	26	0.043		
54	0.271	54	0.038		
106	0.274	109	0.034		
142	0.291	216	0.028		
211	0.309	275	0.027		
262	0.313	375	0.024		
355	0.271	421	0.022		
420	0.252				
490	0.242				

TABLE IV: Effect of Added Xenon on Quantum Yields of Biacetyl Formation^a

^{*a*} Temperature = 26° , acetone pressure = 25.5 Torr.

TABLE V: Effect of Added Ethane on Biacetyl Yields from Acetone^a

Ethane pressure, Torr	0	43	86	171	334	
Φ_{BiA}	0.275	0.276	0.263	0.226	0.171	
^{<i>a</i>} 265.4 nm, temperature = 26° , acetone pressure 25.5 Torr.						

diffusion is inversely proportional to the pressure, then the time required for acetyl radicals to reach the walls is directly proportional to the total pressure. If it is now assumed that in the gas phase acetyl radicals disappear by the firstorder reaction (2)

$$-d(CH_3CO)/dt = k_2(CH_3CO)$$
(9)

and

$$1 - (CH_3CO)_t / (CH_3CO)_0 = 1 - e^{-k_2 a P}$$
(10)

If the fraction of acetyl radicals which disappear on the way to the walls is small the exponential may be expanded in a series and the fraction which remain to reach the walls will be merely $1 - k_2 a P$, where a is a constant. Thus the rate of biacetyl formation will be proportional to $1 - k_2 a P$. This gives the right dependence of biacetyl yield on the pressure. (See Table I.)

As the temperature is raised the value of the rate constant k_2 increases rapidly and quite evidently by about 100° the carbon monoxide yield is unity and no biacetyl is formed.

This analysis of the situation does not prove that biacetyl is formed solely on the walls but the suggestion is strongly supported.

Since biacetyl emission is almost the only emission observed when acetone is irradiated at 313 nm at room temperature, biacetyl must inhibit acetone photolysis by energy quenching. See Table III.

Increase in temperature causes both an increase in the primary quantum yield and an increase in the dissociation of the acetyl radical. At 313 nm the effect on the primary yield is more important in the low-temperature region and biacetyl yields show some increase. The activation energy for dissociation of the acetyl radical is higher⁸ so that dissociation of CH₃CO becomes more important at higher temperatures. Therefore biacetyl yield passes through a maximum at 313 nm but not at 265 nm since at 265 nm the primary yield is much higher.

Some evidence on the magnitudes of the net primary

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yields may be obtained from material balances for methyl and for acetyl radicals. The acetyl radicals either give CO or biacetyl. At 313 nm at room temperature the CO yield is about 0.1 and that of biacetyl is about 0.06. Thus the net primary yield is only about 0.2. At 265 nm CO is about 0.25 and biacetyl is about 0.3 so that the true primary yield is at least 0.85 and may be higher if (6) is important.

An estimate of the primary yield based on the methyl radicals is also possible if one takes the mechanism. Two methyl radicals disappear for each molecule of 2-butanone formed and also for each ethane molecule formed. To a first approximation the primary yield is twice the 2-butanone yield plus the yield of CO and at 313 nm the result is between 0.2 and 0.3 with considerable uncertainty. It should be noted that two methyls are formed per CO molecule. At 265 nm the result is much higher, certainly at least 0.6 but the uncertainty is large. Based on acetyl radical the net primary yield at 265 nm is more than 0.8 and may be unity.

Ethane can be reasonably effective in causing vibrational relaxation but its first excited electronic state is sufficiently high that it cannot produce electronic relaxation. Therefore at 313 nm it should have little effect on the primary dissociation yield of acetone. At 265 nm the primary dissociation yield is quite high. It can therefore be concluded with some uncertainty, that the main effect of added ethane is to retard diffusion of radicals to the walls and that this effect is responsible for the decreased biacetyl yields shown in Table V.

Xenon on the other hand can also induce intersystem crossing by external atom spin-orbit interactions.⁹ At 313 nm dissociation occurs mainly from the singlet state and thus induced intersystem crossing can reduce product yield. At 265 nm dissociation may occur from both singlet and triplet states of acetone. Induced intersystem crossing from the triplet state to upper levels of the ground state could also reduce product yields. Reduced radical diffusion to the walls would also inhibit biacetyl formation. The results shown in Table IV demonstrate that the effect of xenon is indeed complex. It is best to conclude that the effect of xenon on biacetyl yields is not clearly understood.

Thus the results reported are most easily explained in terms of the mechanism presented with the proviso that step 4 leading to biacetyl formation is most probably a wall reaction and that dissociation of the acetyl radical in the gas phase is in competition with diffusion to the walls. The relatively high activation energy of (2) means that the lifetime of the acetyl radical is short enough at temperatures over about 100° that few reach the walls to form biacetyl.

References and Notes

- (1) (a) The authors wish to thank the Robert A. Welch Foundation for a grant in support of this work. The Robert A. Welch Foundation also alded in support of publication costs. (b) On leave from the National Tsing Hua
- (2) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases", Reinhold, New York, N.Y., 1941, pp 356–363.
 (3) W. A. Noyes, Jr., G. W. Porter, and J. E. Jolley, *Chem. Rev.*, 56, 49 (1975)
- (1956).
- (1956).
 (4) The best overall review is in J. G. Calvert and J. N. Pitts, Jr., "Photo-chemistry", Wiley, New York, N.Y., 1964, pp 356–367.
 (5) W. M. Manning, J. Am. Chem. Soc., 56, 2589 (1934).
 (6) See S. Y. Ho, R. A. Gorse, and W. A. Noyes, Jr., J. Phys. Chem., 77, 2000 (1990).
- 2609 (1973).
- (7) D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc., 62, 2052 (1940); J. Heicklen and W. A. Noyes, Jr., *ibid.*, 81, 3858 (1959); J. Heicklen, *ibid.*, 81, 3863 (1959). See ref 2.
- See ref 4 M. R. Wright, R. P. Frosch, and G. W. Robinson, J. Chem. Phys., 33, 934 (1960).