

$\gamma_x$  for biacetyl excited near the 0-0 transition is roughly unity.<sup>16</sup> At shorter wave lengths such as used here it decreases to the extent that photodecomposition from the II'<sup>1</sup>A<sub>u</sub> state (which must be initially formed) and from the first singlet excited state becomes important. Assuming no internal conversion to the ground state and noting that at short wave lengths biacetyl does not fluoresce, then  $\gamma_x \cong 1 - \phi$ , where  $\phi$  is the quantum yield of the primary process. As an estimate for  $\phi$  for the conditions of our experiment the value of 0.34 reported by Bell and Blacet<sup>17</sup> at  $\lambda$  2650 and 100° was used. With  $\gamma_x$  computed in this fashion, Fig. 5 shows a test of eq. III. The results are  $\epsilon_D/\epsilon_A = 770 \pm 80$  and  $K_1\tau_D = 10,000 \pm 1000$ . We did not measure  $\epsilon_D/\epsilon_A$  for benzophenone and for biacetyl in the vapor phase at  $\lambda$  2750 Å. and  $t = 109^\circ$ , but this result appears reasonable. In solutions,  $\epsilon_D/\epsilon_A \cong 600$  at that wave length.

(16) G. B. Porter, *J. Chem. Phys.*, **32**, 1587 (1960).

(17) W. E. Bell and F. E. Blacet, *J. Am. Chem. Soc.*, **76**, 5332 (1954).

If the transfer of energy takes place on every collision

$$K_S = \tau_D(N/1000)r_{DA}^2 [8\pi RT(M_D + M_A)/M_D M_A]^{1/2}$$

where  $r_{DA}^2$  is the sensitizing cross section for biacetyl sensitization and  $M_D$  and  $M_A$  are the molecular weights of the donor and acceptor, respectively. If  $r_{DA}$  is taken to be the sum of the collision radii for such molecules ( $\sim 10$  Å.) then the mean life of the benzophenone appears to be  $\tau_D \cong 1.4 \times 10^{-8}$  sec. or longer. A great deal more work remains to be done on this system, but in principle the qualitative behavior is understood. It is apparent that direct lifetime measurements are becoming necessary and should be undertaken in a systematic way.

A complementary study of the quenching of benzophenone phosphorescence by biacetyl was not undertaken because of the high temperatures necessary to obtain sufficient benzophenone in the vapor phase.

The author wishes to thank Dr. Mary Cox for preparing the quinine bisulfate calibration curve used in this work.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.]

## The Vapor Phase Fluorescence and its Relationship to the Photolysis of Propionaldehyde and the Butyraldehydes<sup>1</sup>

BY R. P. BORKOWSKI<sup>2</sup> AND P. AUSLOOS

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The effects of pressure, temperature and wave length on the fluorescence of *n*-butyraldehyde and isobutyraldehyde have been investigated. At 3340 Å. the fluorescence yield decreases slightly with increase in pressure, while at shorter wave lengths this trend is reversed. Similar observations were made in the case of C<sub>2</sub>H<sub>5</sub>CHO and C<sub>2</sub>F<sub>5</sub>CHO. An increase in temperature reduces the relative fluorescence yields at all wave lengths. Although no phosphorescence was observed, addition of biacetyl leads to a strong emission which could be ascribed to triplet excited biacetyl formed in the energy transfer reaction: A<sup>3</sup> + B → A + B<sup>3</sup> (I). The importance of this process is strongly dependent on wave length and pressure. The analysis of the products formed in the photolysis of *n*-butyraldehyde and *n*-butyraldehyde-biacetyl mixtures indicated that at 3340 Å. the intramolecular rearrangement process, *n*-C<sub>3</sub>H<sub>7</sub>CHO +  $h\nu$  → C<sub>2</sub>H<sub>4</sub> + CH<sub>3</sub>CHO (II), is strongly inhibited by biacetyl. The efficiency of this quenching process parallels that of process I. On the basis of these observations it is concluded that at 3340 Å. process II occurs from a triplet excited state.

### Introduction

Although the photochemistry of the simpler aliphatic aldehydes is now fairly well established,<sup>3</sup> very little information is available in the literature of the emission characteristics of C<sub>2</sub>H<sub>5</sub>CHO, C<sub>2</sub>F<sub>5</sub>CHO, *n*-C<sub>3</sub>H<sub>7</sub>CHO and *i*-C<sub>3</sub>H<sub>7</sub>CHO. The present work was undertaken in order to obtain information about the fluorescence of these compounds as a function of temperature, pressure and wave length, and to correlate these data with the photochemical observations.

### Experimenta

The propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were obtained from Eastman Kodak Co. and were purified on a spinning band distillation column. Only those fractions were used which were shown to be pure on a gas-liquid chromatograph equipped with a flame ionization detector. Acetone (Spectrograde), acetaldehyde and biacetyl were also obtained from Eastman Kodak Co. and

used without further purification. Anhydrous pentafluoropropionaldehyde was obtained from Merck and Co. and used without any further purification. All of these compounds were thoroughly degassed and stored at -80°. The oxygen was assayed reagent grade and was obtained from the Air Reduction Co.

A T-shaped high-quality quartz fluorescence cell with plane windows, 56 mm. long and 28 mm. in diameter, attached to a vacuum line, was used for the fluorescence experiments. The light source was a Hanovia SH-type medium-pressure mercury lamp, used in conjunction with a Bausch and Lomb grating monochromator of 250 mm. focal length with entrance and exit slits 1.0 mm. wide. One light from the monochromator passed through the absorption length of the cell to a 1P28 photomultiplier tube (calibrated against a thermopile at the National Bureau of Standards) for measurement of the transmitted light. The light emitted at right angles to the exciting beam passed through the sidearm of the tee, through the quartz window and a Corning No. 3850 filter, to a second 1P28 photomultiplier tube. The relative fluorescence yields were calculated from the equation

$$Q = (F - F_0)/(I_0 - I_t)$$

where  $F$  is the galvanometer deflection for the emitted light with gas in the cell,  $F_0$  is the deflection for the emitted light with the cell empty,  $I_0$  is the intensity for transmitted light with the cell empty,  $I_t$  is the intensity for transmitted light with gas in the cell.

(1) This research was supported by a grant from the U. S. Public Health Service, Department of Health, Education and Welfare.

(2) National Academy of Sciences-National Research Council Post-doctoral Research Associate 1962-1963.

(3) For a review see: E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I. Reinhold Publishing Corp., New York, N. Y., 1954.

In this paper the emission which is not inhibited by oxygen is designated as fluorescence. The phosphorescence is the difference between the total emission and the fluorescence. The numbers given in Tables II, III, IV, V and VI represent relative emission yields. The absolute yields are approximately 1/100 as large. No correction has been applied to readings made at large absorbed intensities.

The molar extinction coefficients measured at various wave lengths are given in Table I. The maximum of the extinction curves for the unfluorinated aldehydes shifts slightly to longer wave lengths as the length of the alkyl chain is increased. Fluorine substitution also effectively shifts the maximum to longer wave lengths. A similar shift has been noted in the extinction curves for acetone, trifluoro- and hexafluoroacetone.<sup>4</sup> Because of the inaccuracy of the extinction coefficients at 3340 Å. for the unfluorinated aldehydes, the relative emission yields obtained at this wave length may be slightly in error by a constant factor.

TABLE I  
MOLAR EXTINCTION COEFFICIENTS<sup>a</sup> (L./MOLE-CM.)

Compound	Wave length, Å.			
	3340	3130	3025	2804
C <sub>2</sub> H <sub>5</sub> CHO	1.0	8.88	13.3	13.35
<i>n</i> -C <sub>3</sub> H <sub>7</sub> CHO	1.32	9.85	13.36	12.73
<i>i</i> -C <sub>3</sub> H <sub>7</sub> CHO	1.27	10.30	13.58	12.69
CF <sub>3</sub> CHO	3.03	6.97	...	...
C <sub>2</sub> F <sub>5</sub> CHO	8.87	15.25	...	7.87

<sup>a</sup> Measured at 32° except those for CF<sub>3</sub>CHO which were measured at 56°.

The photochemical experiments were conducted with a cylindrical quartz cell (10 cm. in length, 5 cm. in diameter) which was attached to a conventional vacuum system. A Hg-xenon lamp was used as a light source. Its light beam was rendered parallel with a collimating quartz lens and approximately filled the cell. The products were separated by fractional distillation using a Ward still, measured in a Toepler gas buret and subsequently analyzed on a mass spectrometer.

## Results

**Phosphorescence.**—C<sub>2</sub>H<sub>5</sub>CHO, *n*-C<sub>3</sub>H<sub>7</sub>CHO and *i*-C<sub>3</sub>H<sub>7</sub>CHO do not exhibit any measurable triplet state emission at any of the pressures, temperatures or wave lengths used in this investigation. A very weak phosphorescence was observed in the case of C<sub>2</sub>F<sub>5</sub>CHO. This emission, which is considerably smaller than the fluorescence, decreases rapidly with increase in temperature.

**Fluorescence.**—All of the aldehydes which have been investigated fluoresce at yields comparable to those which have been reported for acetone. At 3130 Å., 30°, and a concentration of 4.6 × 10<sup>-3</sup> mole/l. the following values have been obtained for the relative fluorescence yields: CH<sub>3</sub>COCH<sub>3</sub>, 3.8; CH<sub>3</sub>CHO, 2.5; C<sub>2</sub>H<sub>5</sub>CHO, 3.3; C<sub>2</sub>F<sub>5</sub>CHO, 2.8; *n*-C<sub>3</sub>H<sub>7</sub>CHO, 2.8; *i*-C<sub>3</sub>H<sub>7</sub>CHO, 3.0. The results given in Tables II, III, IV and V indicate that in all cases an increase in temperature quenches the relative yield of fluorescence. The effect of concentration on the fluorescence emission at the different wave lengths is as follows:

At 3340 Å. and about 30°, the fluorescence emitted by C<sub>2</sub>H<sub>5</sub>CHO and C<sub>2</sub>F<sub>5</sub>CHO diminishes with increase in concentration. At temperatures above 100°, however, the emission yield is, within experimental error, independent of concentration. At this wave length there is no apparent effect of concentration on the fluorescence emitted by isobutyr-aldehyde. For *n*-butyraldehyde there seems to be a small enhancement of the fluorescence yield with

(4) P. Ausloos and E. Murad, *J. Phys. Chem.*, **65**, 1519 (1961)

TABLE II  
RELATIVE FLUORESCENCE YIELDS OF C<sub>2</sub>H<sub>5</sub>CHO

Concn., moles/ liter × 10 <sup>3</sup>	2804 Å.		3130 Å.			3340 Å.		
	30°	113°	30°	71°	108°	30°	68°	108°
12.2	3.42		3.16			2.88		
8.78	3.33	1.64	3.28	2.32	1.82	2.96	2.33	1.88
6.32	3.12	1.57	3.31	2.37	1.90	2.98	2.37	1.91
4.55	2.94	1.43	3.27	2.38	1.92	3.26	2.61	1.98
3.27	2.63	1.33	3.17	2.31	1.86	3.49	2.59	1.98
2.35	2.43	1.17	3.02	2.17	1.75	3.62	2.63	1.96
1.69	2.26	1.12	2.97	2.16	1.72	3.71	2.54	1.93
1.22	2.08		2.86	2.03	1.63	3.94		
0.88	2.03		2.72	2.08	1.60			
.63			2.55	1.93				
.45			2.60	2.25				
.23			2.67	1.84				
.12								

TABLE III  
FLUORESCENCE AND PHOSPHORESCENCE YIELDS OF  
C<sub>2</sub>F<sub>5</sub>CHO

Concn., moles/l. × 10 <sup>3</sup>	2804 Å.	3130 Å.		3340 Å.	
	31°	31°	122°	31°	122°
A. Fluorescence yields					
6.38	4.00	2.57		1.84	
4.59	4.20	2.85	2.13	1.94	1.49
3.30	4.32	3.10	2.20	2.15	1.41
2.35	4.22	3.34	2.30	2.22	1.51
1.69	4.30	3.46	2.32	2.40	1.52
1.22	3.72		2.34	2.43	1.52
0.88	3.94		2.38	2.56	1.51
0.63	3.58		2.43	2.71	
B. Phosphorescence yields					
6.38	0.35	0.33		0.41	
4.59	.46	.32	0.05	.29	0.13
3.30	.47	.33	.06	.35	.11
2.35	.55	.35	.05	.48	.11
1.69	.46	.41	.06	.51	..

TABLE IV  
RELATIVE FLUORESCENCE YIELDS OF *i*-C<sub>3</sub>H<sub>7</sub>CHO

Concn., moles/l. × 10 <sup>3</sup>	3130 Å.			3340 Å.
	35°	69°	119°	35°
5.73	3.13			3.31
4.19	3.03	2.30	1.76	3.64
3.05	2.92	2.23	1.71	3.58
2.24	2.80	2.19	1.72	3.10
1.61	2.77	2.18	1.72	3.28
1.16	2.78	2.17	1.73	
0.84	2.80	2.24	1.75	
.60	2.86	2.30	1.85	
.43	3.11	2.34	1.85	
.31	3.26	2.47	1.74	
.22	3.58	2.48	1.94	
.16	3.92	2.28	2.12	

increasing concentration. At 3130 Å., about 30°, no appreciable effect of concentration is observed for any of the aldehydes. However, for *n*-C<sub>3</sub>H<sub>7</sub>CHO the fluorescence yield increases slightly with increasing concentration. A similar trend may exist for *i*-C<sub>3</sub>H<sub>7</sub>CHO, at least in the higher concentration range. On the other hand, the opposite trend is observed for C<sub>2</sub>F<sub>5</sub>CHO. For C<sub>2</sub>H<sub>5</sub>CHO the maximum is observed at about 6 × 10<sup>-3</sup> mole/l.

TABLE V  
RELATIVE FLUORESCENCE YIELDS OF  $n\text{-C}_3\text{H}_7\text{CHO}$

Concn., moles/l. $\times 10^3$	3025 Å.	3130 Å.			3340 Å.	
	30°	30°	69°	104°	30°	70°
4.5	2.26	2.84	1.95	..	3.35	2.62
3.3	1.99	2.78	1.95	1.34	3.31	2.78
2.4	1.82	2.59	1.84	1.25	3.24	2.81
1.7	1.73	2.50	1.78	1.19	3.17	2.81
1.06	1.70	2.38	1.73	1.19	3.16	2.94
0.86	1.55	2.31	1.70	1.16		
.62	1.34	2.23	1.65	1.14		
.45	1.39	2.22	1.64	0.98		
.32	1.30	2.14	1.91	.93		
.23		2.46	1.76	.99		

At 3025 and 2804 Å. the fluorescence yields for  $\text{C}_2\text{H}_5\text{CHO}$ ,  $n\text{-C}_3\text{H}_7\text{CHO}$  and  $i\text{-C}_3\text{H}_7\text{CHO}$  increase with increasing concentration. At 2804 Å.  $\text{C}_2\text{F}_5\text{CHO}$  only shows an increase at the lower concentrations, while at concentrations above  $3.3 \times 10^{-3}$  moles/l., the trend is reversed. In this respect  $\text{C}_2\text{F}_5\text{CHO}$  shows the same behavior at 2804 Å. that  $\text{C}_2\text{H}_5\text{CHO}$  shows at 3130 Å. The results of Table II indicate at least in the case of  $\text{C}_2\text{H}_5\text{CHO}$  the effect of concentration at 2804 Å. is of about the same magnitude at 30° and 113°.

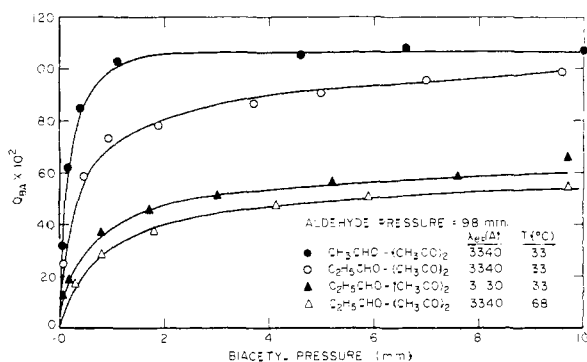


Fig. 1.—Phosphorescence emitted by biacetyl-acetaldehyde and biacetyl-propionaldehyde mixtures.

**Effect of Biacetyl on the Emission.**—As is shown in Figs. 1 and 2, a rather strong phosphorescence emission was observed when relatively small amounts of biacetyl were added to  $\text{C}_2\text{H}_5\text{CHO}$ ,  $n\text{-C}_3\text{H}_7\text{CHO}$  and  $i\text{-C}_3\text{H}_7\text{CHO}$ . Addition of oxygen to any of these mixtures always reduced the emission to the same yield as that observed for the pure aldehydes, indicating that the relative fluorescence yield was not affected by the addition of biacetyl. From the initial slopes of Figs. 1 and 2 it may be concluded that at 3340 Å. and 33° biacetyl is most effective in the case of  $\text{CH}_3\text{CHO}$ <sup>5</sup> and least effective in the case of  $i\text{-C}_3\text{H}_7\text{CHO}$ . At relatively high biacetyl concentrations the emission from  $\text{CH}_3\text{CHO}$ ,  $\text{C}_2\text{H}_5\text{CHO}$  and  $n\text{-C}_3\text{H}_7\text{CHO}$ , respectively, levels off and approaches approximately the same relative value. The plots in Fig. 1 clearly indicate that a decrease in wave length or increase in temperature

(5) The data on  $\text{CH}_3\text{CHO}$  have been included for comparison purposes. An extensive study on the fluorescence and phosphorescence of  $\text{CH}_3\text{CHO}$  has been carried out by C. S. Parmenter and W. A. Noyes, Jr., and will be published shortly.

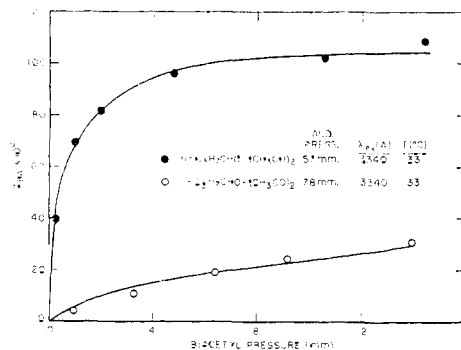


Fig. 2.—Phosphorescence emitted by biacetyl- $n$ -butylaldehyde and biacetyl-isobutylaldehyde mixtures.

has a pronounced reducing effect on the phosphorescence from  $\text{C}_2\text{H}_5\text{CHO}-(\text{CH}_3\text{CO})_2$  mixtures.

Table VI summarizes some of the data obtained on the effect of total pressure for various biacetyl-aldehyde mixtures. A comparison of the phosphorescence observed at 3340 Å. for mixtures containing about 10% biacetyl leads to the interesting observation that an increase in pressure has no effect on the emission of the  $\text{CH}_3\text{CHO}-(\text{CH}_3\text{CO})_2$  mixture but enhances the emission in the case of the other aldehydes. The effect of pressure is apparently much larger for mixtures containing  $i\text{-C}_3\text{H}_7\text{CHO}$  than for those containing  $n\text{-C}_3\text{H}_7\text{CHO}$ , which in turn show a somewhat larger effect than  $\text{C}_2\text{H}_5\text{CHO}-(\text{CH}_3\text{CO})_2$  mixtures. It can also be noticed that the effect of pressure is more pronounced at 3130 Å. than at 3340 Å.

**Effect of Biacetyl on the Primary Decomposition.**—The data of Table VII indicate that at 3340 Å. and 30° addition of biacetyl to  $n\text{-C}_3\text{H}_7\text{CHO}$  quenches the formation of  $\text{C}_2\text{H}_4$ . A plot of the rate of formation of ethylene in absence of biacetyl minus the rate of formation in presence of biacetyl versus the biacetyl pressure is given in Fig. 3.

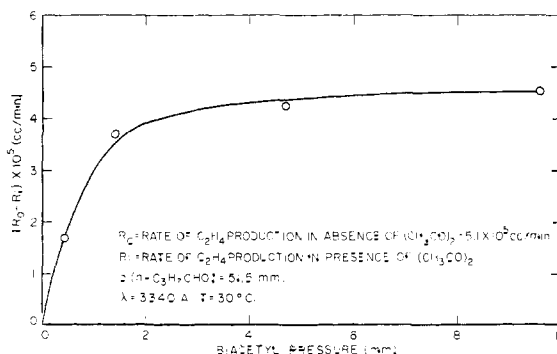


Fig. 3.—Effect of biacetyl on the ethylene formation from the photolysis of  $n$ -butylaldehyde.

## Discussion

**Fluorescence.**—The results of Tables II to V indicate that although the observed variations of the relative fluorescence are rather small, there are two distinct trends which have to be considered: (a) the quenching of the fluorescence with increasing concentration at the longer wave lengths and (b) at the shorter wave lengths the enhancement of the emission with increasing concentration.

TABLE VI  
RELATIVE BIACETYL PHOSPHORESCENCE AS A FUNCTION OF TOTAL PRESSURE FOR VARIOUS BIACETYL-ALDEHYDE MIXTURES

$\lambda_{\text{ex}} = 3340 \text{ \AA.}, T = 33^\circ$													
CH <sub>3</sub> CHO		C <sub>2</sub> H <sub>5</sub> CHO				n-C <sub>3</sub> H <sub>7</sub> CHO		i-C <sub>3</sub> H <sub>7</sub> CHO		C <sub>2</sub> H <sub>5</sub> CHO, $\lambda_{\text{ex}} = 3130 \text{ \AA.}, T = 33^\circ$			
0.112		0.099		0.011		0.167		0.175		0.088		0.008	
p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>	p, mm.	Q × 10 <sup>2</sup>
108	105	108	93	99	72	68	121	94	33	184	76	108	39
78	107	77	95	71	72	49	124	68	28	133	72	99	37
56	108	56	92	52	71	35	121	49	20	95	63	72	30
40	109	40	88	36	67	25	108	35	14	69	53	52	22
29	104	29	86	26	65	18	99	26	10	49	40	37	15
14	106	21	81	19	59	13	95	19	5	25	20	27	10

TABLE VII

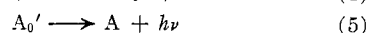
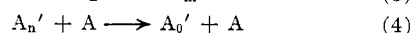
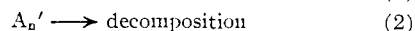
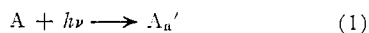
PHOTOLYSIS OF n-C<sub>3</sub>H<sub>7</sub>CHO IN THE PRESENCE OF BIACETYL  
At 3304 Å., T = 30°, p(n-C<sub>3</sub>H<sub>7</sub>CHO) = 51.5 mm.

p (CH <sub>3</sub> CO) <sub>2</sub> , mm.	t, min.	R <sub>CO</sub> × 10 <sup>4</sup> , cc./min.	R <sub>CH<sub>4</sub></sub> × 10 <sup>4</sup> , cc./min.	R <sub>C<sub>2</sub>H<sub>4</sub></sub> × 10 <sup>4</sup> , cc./min.	R <sub>C<sub>2</sub>H<sub>6</sub></sub> × 10 <sup>4</sup> , cc./min.
0	150	1.72	..	0.51	1.72
0.43	150	1.64	0.07	.34	1.96
1.4	150	2.74	.32	.14	1.65
4.7	150	4.86	.45	.084	2.42
9.6	150	8.23	.95	.058	..

Similar effects of concentration on the fluorescence emission have been reported for CH<sub>3</sub>CHO.<sup>6</sup>

It may also be noted that in the case of acetone, self-quenching of the fluorescence and phosphorescence has been reported in an earlier study.<sup>7</sup> More recently,<sup>8</sup> however, no apparent effect of pressure was observed on either the phosphorescence or the fluorescence emitted by acetone at 3130 Å., while at the shorter wave lengths the phosphorescence emitted by acetone shows a pronounced increase with increasing pressure. A similar observation was made in a study carried out in this Laboratory<sup>9</sup> on the phosphorescence emitted by CH<sub>3</sub>COCF<sub>3</sub>. In the latter case it was also shown that at the longer wave lengths the phosphorescence undergoes self-quenching. In this respect the fluorescence emitted by the aldehydes follows similar trends with pressure as the phosphorescence emitted by CH<sub>3</sub>COCF<sub>3</sub> and CH<sub>3</sub>COCH<sub>3</sub>.

The effect of pressure on the fluorescence emission of the aldehydes can be accounted for by the reaction scheme



where A<sub>n</sub>' is an aldehyde molecule in a vibrational level of the excited singlet state, A<sub>0</sub>' an aldehyde molecule in the lowest vibrational level of the upper singlet state, A<sub>m</sub><sup>3</sup>, an aldehyde molecule in an upper vibrational level of the triplet excited state. Step 3 has been included here to account for the presence of triplet excited aldehyde molecules. The pressure effect observed at longer wave lengths for C<sub>2</sub>H<sub>5</sub>CHO and C<sub>2</sub>F<sub>5</sub>CHO necessitates the inclusion of a second-

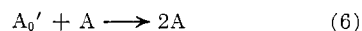
(6) E. Murad, *J. Phys. Chem.*, **64**, 942 (1960).

(7) H. J. Groh, Jr., G. W. Luckey and W. A. Noyes, Jr., *J. Chem. Phys.*, **21**, 115 (1953).

(8) J. Hecklen, *J. Am. Chem. Soc.*, **81**, 3863 (1959).

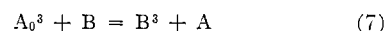
(9) P. Ausloos and E. Murad, *J. Phys. Chem.*, **65**, 1519 (1961).

order process such as



The fact that at the higher temperatures the fluorescence becomes independent of pressure at 3340 Å. is consistent with the occurrence of reaction (6) at low temperatures.

**Effect of Biacetyl.**—It has been demonstrated before<sup>10</sup> that the addition of biacetyl to acetone enhances preferentially the phosphorescence emitted by biacetyl, while the acetone singlet fluorescence efficiency remains unaffected.<sup>11</sup> These observations have been explained by a transfer of excitation energy from acetone to biacetyl.



The validity of this interpretation was corroborated by the fact that addition of biacetyl to acetone also causes a reduction of the primary quantum yield of decomposition of acetone. At relatively high biacetyl concentration, the remaining product yield was ascribed to the decomposition of the upper singlet state of acetone. More recently, a study carried out in the same laboratory<sup>12</sup> on the emission and decomposition yield of diethyl ketone in the presence of varying amounts of biacetyl was interpreted by essentially the same mechanism.

It may be suggested that the results obtained in the present investigation can also be explained by the energy transfer reaction 7.

Figure 1 illustrates that by addition of only 1% of biacetyl to acetaldehyde, a yield of phosphorescence is obtained which does not undergo any further increase with increase in pressure of biacetyl. Also the results of Table VI show that the emission yield in the plateau region is independent of total pressure.

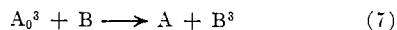
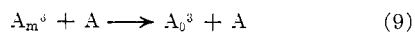
A plot of the phosphorescence emitted by C<sub>2</sub>H<sub>5</sub>CHO-(CH<sub>3</sub>CO)<sub>2</sub> mixtures versus the pressure of biacetyl (Fig. 1) shows that at 3340 Å. the initial slope is less than the one observed for CH<sub>3</sub>CHO, while the efficiency of biacetyl is still smaller for the mixtures containing n-C<sub>3</sub>H<sub>7</sub>CHO and i-C<sub>3</sub>H<sub>7</sub>CHO (Fig. 2). It may, however, be noticed that for the latter two compounds the effect of total pressure on the yield of phosphorescence is also more pronounced. These observations can be accounted for by a competition between the reactions



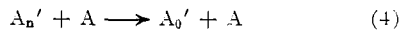
(10) H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

(11) J. Hecklen and W. A. Noyes, Jr., *ibid.*, **81**, 3858 (1959).

(12) D. S. Weir, *ibid.*, **83**, 2629 (1961).



$A_0^3$  represents a low vibrational level of the triplet state. It should be noted that instead of step 3, the following reaction sequence may eventually have to be considered

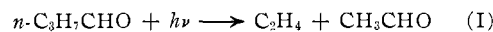


According to the mechanism given above the difference in magnitude of the effect of total pressure for the various mixtures can be accounted for by a variation in dissociative lifetime of the triplet or singlet excited molecule according to the sequence  $i\text{-C}_3\text{H}_7\text{CHO} > n\text{-C}_3\text{H}_7\text{CHO} > \text{C}_2\text{H}_5\text{CHO} > \text{CH}_3\text{-CHO}$ .

If one accepts reaction 3 it may also be expected that the shorter the incident wave length, the higher the degree of vibrational excitation of  $A_m^3$ . It thus follows that a higher pressure will be required to deactivate the triplet aldehyde molecule to the lower vibrational levels from which energy transfer to biacetyl can take place. In agreement with this interpretation is the observation that the phosphorescence emitted by  $\text{C}_2\text{H}_5\text{CHO}-(\text{CH}_3\text{CO})_2$  mixtures is lower at 3130 Å. than at 3340 Å. but is more strongly enhanced by an increase in total pressure at 3130 Å. than at 3340 Å. In this connection it may be noted that recent measurements of the phosphorescence emitted by  $\text{CH}_3\text{COCH}_3$ <sup>8,9</sup> and  $\text{CH}_3\text{COCF}_3$ <sup>9</sup> did show that at the lower incident wave length the emission is enhanced rather strongly by increasing the pressure. These observations, which have been accounted for by a very similar mechanism,<sup>8</sup> indicate that the *absence* of any phosphorescence or *effect of biacetyl* is not necessarily proof that only molecules excited to an upper singlet state undergo decomposition, but can just as well be explained by the formation of molecules excited to high vibrational levels of the triplet state in process 3. It is obvious, however, that the effects of pressure at the different wave lengths could equally well be explained by reactions 4 and 11. From the data presented in this paper it cannot be deduced what fraction of the aldehyde molecules excited to the upper singlet state undergo a transition to the triplet state. The rather small effect of wave length and structure on the relative fluorescence yield for the various aldehydes would seem to indicate that the importance of reaction 3 or 11 does not undergo any drastic variations. This is corroborated by the fact that at 3340 Å. the maximum phosphorescence yield emitted by biacetyl is of the same order of magnitude in mixtures containing  $\text{CH}_3\text{CHO}$ ,  $\text{C}_2\text{H}_5\text{CHO}$  and  $n\text{-C}_3\text{H}_7\text{CHO}$ , respectively.

**The Effect of Biacetyl on the Primary Decomposition.**—It is well known<sup>13</sup> that by absorption of a photon  $n\text{-C}_3\text{H}_7\text{CHO}$  undergoes an intramolecular rearrangement resulting in the elimination of ethylene.

(13) F. E. Blacet and J. G. Calvert, *J. Am. Chem. Soc.*, **73**, 661 (1951).

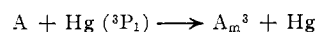


The yield of ethylene should at reasonably low conversions not be affected by secondary reactions and may consequently be considered as a reliable measure of the relative quantum yield of process I. The fact that at 3340 Å. biacetyl reduces the relative rate of formation of  $\text{C}_2\text{H}_4$  by nearly a factor of ten indicates that process I can be readily quenched by biacetyl. It may consequently be concluded that an excited triplet aldehyde molecule is involved in process I. The correlation between the quenching of the primary decomposition and the formation of the triplet excited biacetyl is demonstrated by the plot  $(R_0 - R_i)$  given in Fig. 3 which levels off at about the same pressure of biacetyl as the phosphorescence which is presented in Fig. 2. The fact that addition of biacetyl does not appreciably affect the yield of propane may be considered as an indication<sup>14</sup> the dissociative process



occurs from a singlet electronic state and/or from a triplet electronic state excited to a high vibrational level.

Recent observations<sup>15</sup> seem to contradict our conclusion that the olefin elimination process at 3340 Å. occurs by way of a triplet excited molecule. It has indeed been suggested by Borrell and Norrish that in view of the very low yield of ethylene<sup>16</sup> observed in the mercury-sensitized decomposition of  $n\text{-C}_3\text{H}_7\text{CHO}$ , as compared to the direct photolysis, only aldehyde molecules excited to the upper singlet state can undergo process I. The latter conclusion was based on the Wigner spin conservation rule. If we accept that this selection rule does hold for heavy atoms, the triplet aldehyde molecule formed in the process



can be expected to be in a much higher energy level than the one produced at 3340 Å. This may lead to a considerably higher relative probability of the dissociative process II, which is energetically less favorable than the intramolecular rearrangement process I. On this basis all one can deduce from a comparison of the products formed in sensitized and non-sensitized decomposition is that decomposition of a molecule excited to a high vibrational level of the triplet state may not contribute appreciably to the formation of ethylene. Considering the information which is available at present it may be tentatively suggested that the occurrence of process I by way of an excited triplet state prevails at the longer wave lengths, while an excited singlet state may contribute to the decomposition at the shorter wave lengths.

(14) As evidenced by the formation of methane at high biacetyl concentrations, direct decomposition of biacetyl becomes important and complicates the reaction mechanism.

(15) P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A262**, 19 (1961).

(16) A few sensitized experiments which were carried out in this Laboratory did show that the yield of ethylene is smaller than in the direct photolysis, but by no means negligible. At 30° a value of 0.08 was obtained for the ratio  $\text{C}_2\text{H}_4/\text{CO}$ . From the pressure dependence on the rate of formation of  $\text{C}_2\text{H}_4$  it could be concluded that the ethylene was mainly formed by a sensitized decomposition.