

swings in a pair of electrons and forms a double bond with the aluminum atom. This type of resonance is not expected to occur to the same degree for halogen atoms forming two bonds, which accounts for the fact that the observed  $Al_2-X_3$  distances are nearly equal to the sum of the appropriate radii.

It is interesting to note that the observed values of the  $Al_2-X_3$  distances show a greater tendency for the chlorine and bromine atoms to form double bonds than of iodine atoms; this is compatible with the results of other investigations.

We wish to express our thanks to Professor Linus Pauling for his aid and helpful criticism during the course of this investigation.

### Summary

It is shown that in the gaseous state the dimeric

molecules of aluminum chloride, bromide, and iodide consist of two tetrahedra sharing an edge with six halogen atoms at the corners, each tetrahedron containing one aluminum atom. The final values of the interatomic distances are as follows

The subscripts on the atomic symbols refer to their positions in the molecule as given in Fig. 1.

	$Al_2Cl_6$	$Al_2Br_6$	$Al_2I_6$
$Al_1-Al_2$	$3.41 \pm 0.20 \text{ \AA.}$	$3.39 \pm 0.10 \text{ \AA.}$	$3.24 \pm 0.15 \text{ \AA.}$
$Al_2-X_3$	$2.06 \pm .04$	$2.21 \pm .04$	$2.53 \pm .04$
$Al_2-X_5$	$2.21 \pm .04$	$2.33 \pm .04$	$2.58 \pm .04$
$Al_2-X_6$	$4.77 \pm .15$	$4.93 \pm .10$	$5.22 \pm .15$
$X_3-X_4$	$3.53 \pm .04$	$3.72 \pm .03$	$4.20 \pm .03$
$X_3-X_5$	$3.56 \pm .02$	$3.78 \pm .03$	$4.24 \pm .02$
$X_5-X_6$	$2.83 \pm .10$	$3.20 \pm .10$	$2.90 \pm .15$
$X_3-X_7$	$5.49 \pm .05$	$5.76 \pm .10$	$6.24 \pm .15$
$X_5-X_6$	$6.52 \pm .05$	$6.86 \pm .10$	$7.54 \pm .10$

PASADENA, CALIF.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## Photochemical Studies. XXVI. A Further Study of the Fluorescence of Acetone Vapor and its Relationship to the Photochemical Decomposition

By MAX S. MATHESON AND W. ALBERT NOYES, JR.

The fluorescence of acetone vapor was reported by Damon and Daniels,<sup>1</sup> who stated that it is greenish and is changed to blue by the presence of small amounts of oxygen. The oxygen disappears during illumination and this fact has been used as a means of determining small amounts of this substance.<sup>2</sup>

Two regions, one extending from 4100 to 4820  $\text{\AA.}$  (maximum 4580  $\text{\AA.}$ ) and the other from 4990 to the limit of plate sensitivity (5210  $\text{\AA.}$ ), were found by Damon and Daniels.<sup>1</sup> Norrish, Crone and Saltmarsh<sup>3</sup> report three bands of fluorescent emission (all diffuse) with maxima at 5117, 5572 and 6095  $\text{\AA.}$  More recently Padmanabhan<sup>4</sup> has found that the bands are not devoid of structure but consist of diffuse bands superimposed upon a continuous spectrum. Ten bands, two considered to be doubtful, were reported.

Herzberg<sup>5</sup> first found a discrete structure in the near ultraviolet absorption of acetone vapor and

this has been confirmed by other workers.<sup>3,6</sup> The detailed analysis of these bands and their interpretation is still lacking, but the existence of such a structure is in conformity with the fact that fluorescence is observed. However, structure is difficult to observe in many polyatomic molecules even though fluorescence is found. Such seems to be the case with ethyl methyl ketone<sup>7</sup> and diethyl ketone.<sup>8</sup>

All authors who have studied the quantum yield of acetone decomposition in the near ultraviolet at room temperature agree that it is low.<sup>9</sup> The explanation of this fact is not complete. Damon and Daniels<sup>1</sup> state that the fluorescence is too weak to be the primary cause of this effect. However Fisk and Noyes<sup>10</sup> studied the fluorescence excited by the 3130  $\text{\AA.}$  line of mercury and found (with the very low intensities used) a Stern-Volmer mechanism to be obeyed. At moderate pressures it was found that the number of quanta absorbed was roughly equal to the sum

(1) Damon and Daniels, *THIS JOURNAL*, **55**, 2363 (1933).

(2) Damon, *Ind. Eng. Chem., Anal. Ed.*, **7**, 133 (1935); Fugassi, *THIS JOURNAL*, **59**, 2092 (1937); Fugassi and Daniels, *ibid.*, **60**, 771 (1938).

(3) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

(4) Padmanabhan, *Proc. Ind. Acad. Sci.*, **5A**, 594 (1937).

(5) For mention see Scheibe, Povenz and Linström, *Z. physik. Chem.*, **20B**, 292 (1933).

(6) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934); Noyes, *Trans. Faraday Soc.*, **33**, 1495 (1937).

(7) Duncan, Ells and Noyes, *THIS JOURNAL*, **58**, 1454 (1936).

(8) J. W. Zabor, M.S. Thesis, Brown University, 1938.

(9) See refs. 1 and 3, Leermakers, *THIS JOURNAL*, **56**, 1900 (1934).

(10) Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).

of the three quantities: (a) number of molecules which fluoresce; (b) number of molecules which dissociate; (c) number of activated molecules deactivated by collision. However, the mechanism used to accomplish this balance disagreed quite definitely with some of the photochemical facts, particularly with the supposed decrease in quantum yield with acetone pressure.

That the mechanism of acetone photodecomposition may be quite complex is suggested by the work of Spence and Wild.<sup>11</sup> These authors find approximately one molecule of carbon monoxide for each molecule of ethane at 3130 Å., but a considerable deficiency of carbon monoxide at shorter wave lengths. This agrees with the fact, first reported by Barak and Style,<sup>12</sup> that appreciable amounts of biacetyl are formed at room temperature during photodecomposition of acetone. At 60° the amount of biacetyl was found to be negligible, due perhaps to the instability of the CH<sub>3</sub>CO radical at that temperature.

To attempt to elucidate the phenomenon of a low quantum yield coupled with a relatively small amount of fluorescence it was thought desirable to study the fluorescence over as wide a range of conditions as practicable. Unfortunately the absorption coefficient of acetone is so low at 3130 Å. that it did not prove feasible to use pressures low enough to permit a decision to be made as to the effect of collisions on this reaction.

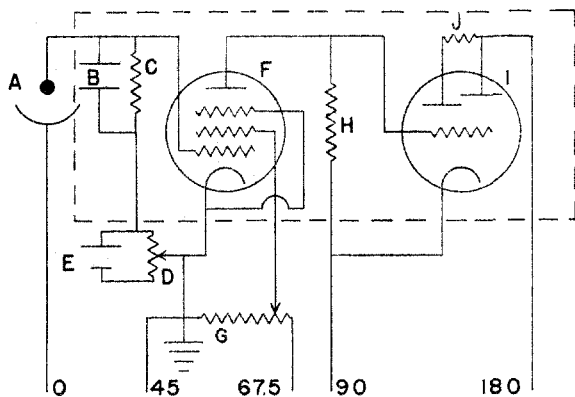


Fig. 1.

### Experimental

**Purification of Acetone.**—Reagent quality acetone was purified by the method of Shipsey and Werner<sup>13</sup> by crystallizing from an acetone solution of anhydrous sodium

iodide. The acetone was distilled from the salt over a steam-bath and then carefully fractionated, the middle portion boiling at 55.8° (uncorr.) being retained. After placing in the vacuum line, it was refluxed for forty-eight hours over boron trioxide at low temperatures and then fractionated. No stopcocks or joints involving grease were present in the line.

**Purification of Biacetyl.**—Biacetyl (Eastman) was fractionally distilled three times, the final middle fraction boiling at 87–88° being retained. After placing in the vacuum line, it was subjected to five low pressure fractionations at room temperature, the first three condensations taking place at liquid air temperatures and the last two with dry ice.

**The Fluorescence Cells.**—Two all-quartz cells having a T shape were used at different times. These were sealed to the rest of the line with graded seals. The length of the main limb was 4 cm. and the windows were 2 cm. in diameter.

**The Light Source.**—A General Electric H3 quartz high pressure mercury arc operated at 85 watts was used. A hole was blown in the glass envelope surrounding the arc to permit the exit of wave lengths below 3500 Å.

The light was passed through a water-cooled Red Purple Correx A filter and then through either one or two quartz plates lightly silvered (by sputtering) according to the directions given by R. W. Wood.<sup>14</sup> A quartz lens was used to bring the radiation to a focus at the center of the cell, although the beam was nearly parallel.

The radiation transmitted by the optical system was photographed with an E3 Hilger spectrograph on Eastman 33 plates. Microphotometer tracings<sup>15</sup> showed the following distribution of radiation: (a) 3130 Å., 79%; (b) 3340 Å., 8%; (c) 3650 Å., 12%; (d) all others less than 1%. (No trace of lines below 3130 Å. could be found on the plates which were microphotometered.)

**The Measurement of the Incident Radiation.**—For some runs the incident radiation was measured by a cesium oxide photoelectric cell with quartz envelope. For others a similar cell with Pyrex envelope was used. One or the other of these cells was placed on the exit side of the long limb of the T so that transmitted radiation was measured.

The current from this photoelectric cell was amplified and measured by the circuit shown in Fig. 1.<sup>16</sup> The photoelectric cell is shown at A. F is a Sylvania type 77 vacuum tube. I is a 6E5 magic eye radio tube. D is a student potentiometer. C is a 10-megohm composition resistor and B is a 0.1 microfarad condenser. H is a 1 megohm composition resistor and J is a 0.5 megohm composition resistor. G is a 10<sup>8</sup>-ohm screen potentiometer. E is a battery of three dry cells. The figures at the bottom refer to voltages obtained by the use of four B batteries.

This amplifier was used as a null point indicator, the null point used being the just closed condition of the fan-shaped shadow on the fluorescent screen of the 6E5 tube (I). The change in the reading of the student potentiometer D necessary to just close the shadow gave a measure

(14) Wood, "Physical Optics," The Macmillan Co., New York, N. Y., 1929, p. 15.

(15) The authors wish to express their appreciation to Professor W. W. Watson of Yale University for his kindness in having the microphotometer tracings made.

(16) J. W. Tokey, M.S. Thesis, Brown University, 1937.

(11) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

(12) Barak and Style, *Nature*, **135**, 307 (1935); see Spence and Wild, *ibid.*, **138**, 206 (1936).

(13) Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1933)

of the intensity of light falling on the photoelectric cell. The linearity of amplification was tested by use of the inverse square law of intensities obtained from a filament lamp placed at distances of two meters or greater.

Since the fraction of radiation transmitted by the exit window of the fluorescence cell was constant, it was possible to calculate quantities proportional to the incident intensity with the use of the known absorption coefficients of acetone vapor.<sup>17</sup> Absorption of the mercury line at 3130 Å. was alone considered.

**The Measurement of the Fluorescent Radiation.**—The fluorescent radiation was measured by a photoelectric cell with quartz envelope and having a plane window in front of the cathode. Current from this photoelectric cell was measured with a DuBridge circuit using an FP54 tube.<sup>18</sup>

**Sample Experiment.**—The method of introducing acetone from a cooled reservoir until it reached the desired pressure was used previously.<sup>10</sup> Biacetyl, when used, was introduced from calibrated volumes where the pressure was known. At low pressures the ratio of pressures could be determined exactly even if the absolute pressure was uncertain.

Both amplifiers and the arc were turned on and a half hour allowed to elapse in order to obtain steady conditions. The DuBridge and Brown<sup>18</sup> amplifier was balanced as described by these authors in order to minimize the drift of the galvanometer.

A shutter in front of the light source prevented any decomposition of acetone vapor while the pressure of the latter was being adjusted. Since the DuBridge and Brown amplifier had a lag of about three minutes, the transmitted and the fluorescent radiation were both measured over an interval of four or five minutes at least. Table I shows a sample set of readings.

TABLE I  
DATA OF A TYPICAL EXPERIMENT

Time	$G_f$	$G_t$	Operation
3:33 P. M.	-11.40	1078.0	Light shut off from cell
3:34	-11.40 (-11.40)	1078.5	(Pressure acetone = 152.8 mm.)
3:35	+14.00 (13.99)	972.0	Light on, $P = 152.8$ mm.
3:36	14.72 (14.69)	971.0	
3:37	15.12 (15.08)	971.5	
3:38	14.99 (14.93)	972.0	
3:39	4.20 (4.13)	956.0	Light on, $P = 0$ (liquid air on trap)
3:40	3.25 (3.17)	954.5	
3:41	3.00 (2.90)	954.5	
3:42	3.05 (2.94)	954.5	
3:43	-10.70 (-10.83)	1077.5	Light off
3:44	-11.20 (-11.34)	1077.5	
3:45	-11.25 (-11.40)	1077.5	

$G_f$  is measure of fluorescence intensity.  $G_t$  is obtained from measurements of transmitted intensity.

Under  $G_f$  it is seen that a drift of the readings toward more positive values has taken place during the experiment. Experimentally this drift was found to be nearly uniform. The drift per minute is, therefore, (11.40-11.25)/11. The fig-

(17) Porter and Iddings, *THIS JOURNAL*, **48**, 40 (1926).

(18) DuBridge and Brown, *Rev. Sci. Instruments*, **4**, 532 (1933).

ures under  $G_f$  are then corrected for drift with the results given in parentheses. The value 14.93 obtained at 3:38 is due to scattered plus fluorescent radiation, while the value 2.94 obtained at 3:42 is due to scattered radiation alone. The difference (11.99) is proportional to the intensity of the fluorescence. At low acetone pressures the scattered radiation may be a large fraction of the total measured, so that the accuracy is small.

The average of  $G_t$  at 3:34 and 3:44 is 1078.0 and is the value with the light off. By subtracting the reading at 3:42 one obtains 123.5, which is proportional to the radiation transmitted when no acetone is in the cell.

Since the amount of 3130 Å. radiation absorbed is small it will vary nearly linearly with the path length. From the geometry of the system the length of path from which radiation could be incident on the photoelectric cell measuring the fluorescence is 2.8 cm., but since relative results only are necessary this figure is not very critical.

Let  $A$  be the fraction of the radiation transmitted by the back window,  $D_t$  the measured intensity at 0 acetone pressure (= 123.5 above),  $D_t'$  the intensity in front of the back window and  $D_t''$  the intensity in back of the front window both with acetone in the cell.

Then

$$D_t'' = D_t/A \quad (1)$$

From Beer's law

$$D_t' = D_t'' \exp(-kcl) = D_t/A \exp(-kcl) \quad (2)$$

where  $l$  is the cell length (4 cm.),  $c$  is the concentration in moles per liter and  $k = 6.63$  for 3130 Å. radiation.<sup>17</sup> Using the perfect gas law one finds (omitting  $A$  which is constant)

$$D_t' = D_t \times 10^{-61.735 \times 10^{-5}P} \quad (3)$$

where  $P$  is in millimeters.

The effective path (2.8 cm.) begins 0.5 cm. back of the front window. Use of Beer's law indicates that the absorbed intensity is given by

$$I_a = D_t \times 10^{-61.735 \times 10^{-5}P} (10^{5.41 \times 10^{-4}P} - 10^{0.996 \times 10^{-4}P}) \quad (4)$$

where the quantity in parentheses is the fraction of the light absorbed in the effective path (2.8 cm.).

In the above example

$$I_a = 17.28 \quad (5)$$

and

$$I_a/I_t = 1.44 \text{ (at } P = 152.8 \text{ mm.)} \quad (6)$$

A series of values of  $I_a/I_t$  could be made. As shown previously<sup>10</sup> the intensity units cancel

when a plot is made of this quantity against the pressure and the slope is divided by the intercept.

The estimated accuracy of  $I_a/I_f$  is about  $\pm 5\%$ , although this tends to increase at low pressures of acetone where the fluorescence is very weak.

When biacetyl was mixed with the acetone or used alone the procedure was exactly similar to that described above, except that with pure biacetyl the fraction of light absorbed was assumed to be proportional to the pressure since accurate absorption coefficients of this substance have not been obtained.

### Discussion of Results

It should be kept in mind that the incident intensity in the present work was much larger (100 to 1000 times) than that used in the previous experiments.<sup>10</sup>

Since it was the object of the present work to ascertain what effect collisions have in deactivating acetone molecules, values of  $I_a/I_f$  were desired over a large pressure range and particularly at low pressures. However, it became evident quite early that measurements below pressures of 1 to 2 cm. were unreliable due to the small absorption by the acetone and consequent weak fluorescence.

Attempts to verify the previous work<sup>10</sup> at higher pressures by plotting  $I_a/I_f$  against pressure and dividing the slope by the intercept gave not only results differing from those published, but the results were erratic and not reproducible. Figure 2 shows plots of  $I_a/I_f$  vs.  $P$  (cm.) for two different runs in which each point involved an exposure of the acetone to the radiation during ten minutes. Both of these runs were made by starting at low acetone pressures and adding acetone for each successive point without, however, evacuating the line between points.

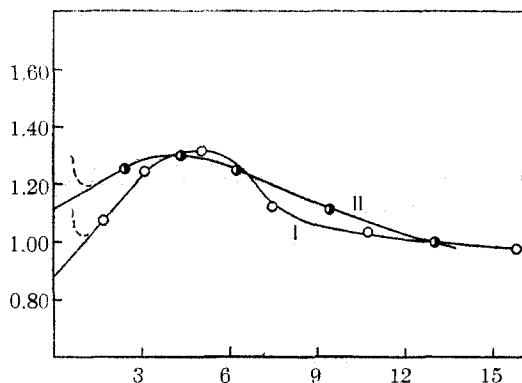


Fig. 2.

As stated above, experiments at low pressures are accompanied by a large error, although it may be significant that  $I_a/I_f$  apparently increased at pressures of a centimeter or below as indicated roughly by the dotted lines.

In the previous work it was found that

$$\text{Slope/Intercept} = 0.052 (\text{Av.})^{10} (P \text{ in cm.}) \quad (7)$$

In the present experiments many values of slope/intercept were found which agree approximately with this figure providing one considers only points at low pressures obtained before the acetone had been subjected to a long exposure to the radiation. Thus in Fig. 2, 0.134 and 0.036 (approximately) were obtained for slope/intercept for the lower points. It seems evident that the conclusions of Fisk and Noyes<sup>10</sup> need not be seriously modified, although they were based on data obtained over a limited range of experimental conditions.

However, it should be pointed out that in every case the  $I_a/I_f$  vs. pressure curve passes through a maximum (see also Fig. 3). Although the data obtained previously indicate that the slope tends to become less at higher pressures, this fact had not been observed.

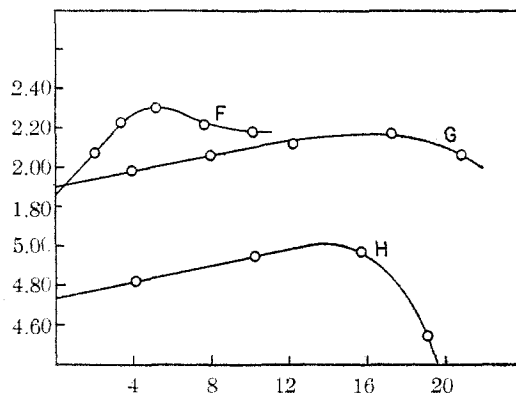


Fig. 3.—F, 2-minute exposure; G,  $D_t$  one-fourth that for F, same exposure time; H,  $D_t$  same as for F, 4-minute exposure, fresh acetone used for each point.

The following observations are also important:

(1) As the intensity is increased the value of  $I_a/I_f$  decreases, this effect being more noticeable with long than with short exposures. Previously it had been found (for very low intensities) that  $I_a/I_f$  was approximately independent of intensity, although the data were not very satisfactory on this point.

(2) At a given pressure and a given intensity  $I_a/I_f$  decreases with increasing time. However, if

the acetone is condensed with liquid air the value of this ratio returns almost exactly to its initial value. This indicates that some relatively non-volatile substance is responsible for this phenomenon, since the mere interposition of a shutter did not produce this effect.

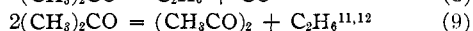
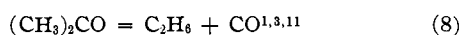
(3) When short exposures were used for the measurement of each point (curves F, H and G, Fig. 3) the point of inflection tended to come at higher pressures than was the case with long exposures. A greater displacement was observed with low intensities (curve G). (It should be kept in mind that with the exception of H (Fig. 3) successive points were obtained by adding acetone without intervening evacuation.)

(4) If the line was evacuated between successive points (curve H, Fig. 3) the maximum was displaced toward higher pressures even though high intensities were used.

(5) Results obtained by starting at a high pressure and removing acetone to reduce the pressure between points did not agree with those obtained by the procedure normally used.

All of these facts point to the formation during illumination of some substance which has a marked effect in increasing the fluorescence.

Neglecting secondary reactions of relatively minor importance at room temperature, the photochemical decomposition of acetone proceeds mainly in two ways



(In the presence of water Damon and Daniels<sup>1</sup> state that diacetone alcohol may be formed.)

Of the products in (8) and (9) biacetyl would be the least volatile and from other considerations might be expected to be the one responsible for the phenomena discussed above. It was decided, therefore, to examine the effect of biacetyl on the fluorescence of acetone.

Table II presents results obtained during one run in which the acetone pressure and the incident intensity were maintained nearly constant.

TABLE II  
EFFECT OF DIACETYL ON FLUORESCENCE OF ACETONE

Acetone press., mm.	69.6	69.8	69.0	69.2	69.9	70.7	68.7
Biacetyl press., mm.	0.50	0.34	0.23	0.16	0.11	0.07	0
<i>I</i>	29.08	23.22	24.05	25.68	25.24	25.41	4.68
( <i>D</i> )	148.0	142.0	141.0	137.5	135.3	135.75	133.0
<i>D<sub>t</sub>/I<sub>t</sub></i>	5.1	6.1	5.9	5.4	5.4	5.3	28.4

(*D<sub>t</sub>/I<sub>t</sub>* is very closely proportional to *I<sub>a</sub>/I<sub>t</sub>*)

Biacetyl alone at the pressures shown in Table II would absorb an amount of radiation too small to measure and yet it seems to increase the apparent amount of fluorescence five or sixfold. This large effect at once raises the question as to whether acetone itself fluoresces.

The decisive answer to the question here raised cannot be made at once, but the following facts point to a fluorescence of acetone itself:

(1) After condensation by liquid air the fluorescence diminishes and reproduces the value obtained at the beginning of illumination. Several minutes of illumination are necessary, except at higher acetone pressures where the absorption is high, before the fluorescence begins to increase markedly.

(2) The fluorescence changes from green to blue when oxygen is present.<sup>1</sup> The interpretation of this fact is tentative and will be discussed later.

The conclusions to which the above experimental evidence seemed to lead necessitated an investigation of the fluorescence spectrum. The spectrum was photographed both with a small Hilger glass prism spectrograph and with an E3 spectrograph with glass train. The silvered quartz plates were removed from the optical system (see above) so that the incident radiation was less monochromatic than in the rest of the experiments. Cramer Iso Presto and Wratten and Wainwright panchromatic plates were used.

The following results were obtained:

(1) With pure acetone (102 mm.), frozen down every seven minutes to lessen the effect of biacetyl and a three-hour exposure with the small spectrograph, two bands at approximately 5100 and 5600 Å. were observed. These are almost certainly the bands at 5117 and 5572 Å. reported by Norrish, Crone and Saltmarsh.<sup>3</sup> When photographed with the larger spectrograph the band at 5117 Å. seemed to consist of several maxima as found by Padmanabhan.<sup>4</sup>

(2) With pure biacetyl (45 mm.), two-hour exposure with the small spectrograph, the same bands as in (1) appeared and in addition a faint band about 6100 Å. The latter is probably the band at 6095 Å. reported by Norrish, Crone and Saltmarsh.<sup>3</sup>

(3) Acetone (65 mm.) and biacetyl (0.5 mm.) and a two-hour exposure with the small spectrograph showed the same bands as in (1).

No trace of the region extending from 4100 to 4800 Å. reported by Damon and Daniels<sup>1</sup> could be

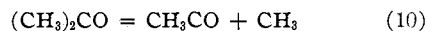
found, but this means in all probability that it is weak compared to the fluorescence at longer wave lengths. (The plates used by Damon and Daniels were not sensitive at wave lengths longer than 5200 Å.) The blue color of the fluorescence when oxygen is present indicates that wave lengths below 5000 Å. must be present. The observed bands at longer wave lengths, which were alone observed by Norrish, Crone and Saltmarsh,<sup>3</sup> are evidently much more intense than any fluorescent emission in the blue region.

These results seem to indicate beyond any question that the supposed emission of acetone is the same as that of biacetyl with the possible exception of wave lengths below 5000 Å. The effect of oxygen on the fluorescence of biacetyl and of acetone was observed visually. With acetone oxygen weakened the fluorescence considerably and changed its color from greenish to blue in agreement with the results of Damon and Daniels.<sup>1</sup> With biacetyl the fluorescence was weakened and became less yellow although it did not acquire the characteristic blue of acetone. At the same time biacetyl gave a heavy deposit on the windows.

If the emitter is the same for both biacetyl and acetone the following possibilities suggest themselves:

(1) Acetone may dissociate into CH<sub>3</sub> and CH<sub>3</sub>CO, the latter being either formed in an excited state or raised to an excited state by collisions of the second kind with excited molecules. Biacetyl would perhaps dissociate to give two CH<sub>3</sub>CO radicals.

The energy required to dissociate acetone by the equation



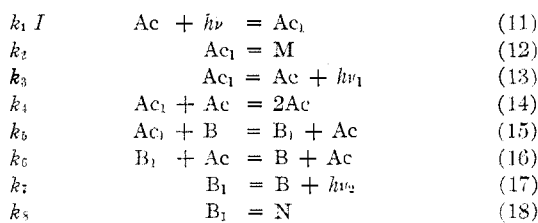
is uncertain, but is probably not less than 75 kcal. Quanta of 3130 Å. radiation correspond to about 91 kcal. per mole. Thus neither free radical could possess enough potential energy to be capable of fluorescing in the visible spectrum (approximately 50 kcal. per mole would be required at 6000 Å.). Roughly the same discrepancy would exist for dissociation and subsequent fluorescence of biacetyl.

Thus if emission by the CH<sub>3</sub>CO radical takes place this must follow an activation by a collision of the second kind. A detailed mechanism considering the possible secondary reactions leads to a kinetic expression too complex to be capable of any sort of rigorous test. The enhancement of the fluorescence due to the addition of small

amounts of biacetyl would have to be due to the dissociation of the latter into CH<sub>3</sub>CO radicals by collisions of the second kind with excited acetone. Thus two excited acetone molecules would be necessary in each sequence of events leading to fluorescence. Whether or not the incident intensity would appear as the square in the expression for the fluorescent intensity would depend on other steps used in the mechanism.

(2) The major portion of the fluorescence may be due to excited biacetyl molecules. This substance absorbs<sup>19</sup> at least to 4700 Å. If excited biacetyl molecules are reduced to the zero vibration level by collisions prior to fluorescence,<sup>20</sup> the operation of the Franck-Condon principle *might* cause the maximum intensity of fluorescent emission to lie at longer wave lengths than the long wave absorption limit at room temperature.

If (2) is the correct explanation, the effect of oxygen is to prevent the formation of biacetyl and the weak blue fluorescence observed with oxygen present<sup>1</sup> would be due to acetone itself. The second explanation may be expressed by the following mechanism



Ac represents a normal and Ac<sub>1</sub> an excited acetone molecule. B is a normal and B<sub>1</sub> an excited biacetyl molecule. M and N are dissociation products. These equations lead to

$$I/I_t = \frac{(k_2 + k_3 + k_4(\text{Ac}) + k_5(\text{B}))(k_6(\text{Ac}) + k_7 + k_8)}{k_1 k_3 (k_6(\text{Ac}) + k_7 + k_8) + k_1 k_5 k_7 (\text{B})} \quad (19)$$

Since biacetyl has a very large effect on the fluorescence, this equation probably reduces to

$$k_1 I/I_t = (k_6(\text{Ac}) + k_7 + k_8)/k_7 \quad (20)$$

and  $I/I_t$  is independent of biacetyl pressure unless the latter is very low. This is in accord with the facts.

In order to find an expression for the effect of intensity and time on the ratio of  $I/I_t$ , it is necessary to introduce a rate of biacetyl formation. If this is assumed to be of such a nature that

$$(\text{B}) = KI_0(\text{Ac})t \quad (21)$$

(19) Cf. Sponer, "Molekülspektren," Verlag von Julius Springer, Berlin, 1935, Vol. 1, p. 117.

(20) Cf. Gradstein, *Z. physik. Chem.*, **22B**, 384 (1933).

where  $I_0$  is the incident intensity and  $t$  is the time, equation (19) becomes

$$I/I_t = \frac{(k_2 + k_3 + k_4(\text{Ac}) + k_5KI_0(\text{Ac})t)(k_6(\text{Ac}) + k_7 + k_8)}{k_1k_3(k_6(\text{Ac}) + k_7 + k_8) + k_1k_5k_7KI_0(\text{Ac})t} \quad (22)$$

This equation is a quadratic in (Ac) divided by a first order expression in (Ac) and may be made to fit the data presented. When  $I_0t$  is very small, (22) reduces to

$$k_1I/I_t = 1 + (k_2 + k_4(\text{Ac}))/k_3 \quad (23)$$

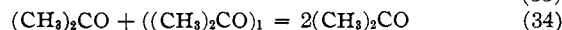
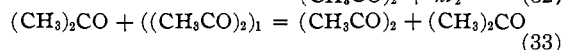
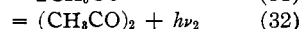
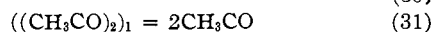
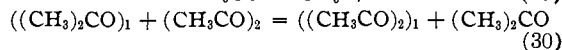
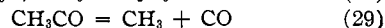
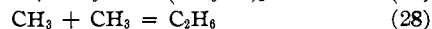
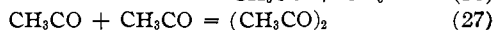
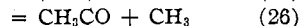
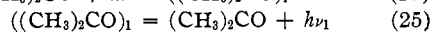
which is the equation used by Fisk and Noyes.<sup>10</sup>

Therefore it is possible to explain the observed facts by means of the mechanism included in equations (11) to (18), but it is unsafe to conclude that fluorescence of the acetyl radical does not take place or may not be mainly responsible for the phenomena described.

The Raman spectrum of biacetyl has not been investigated very completely.<sup>21</sup> Except, possibly, for the line at 1725 cm.<sup>-1</sup>, no close agreements are found with differences in wave numbers among the bands found by Padmanabhan.<sup>4</sup> However, this is not evidence at present against the interpretation given since the electronic spectrum of this molecule has not been analyzed.

Acetone seems to have no effect on the fluorescence of biacetyl, when the latter is at a pressure of about 50 mm. and the former at a pressure of a few millimeters. Thus the seemingly good resonance for deactivation of acetone by biacetyl does not carry over to the deactivation of biacetyl by acetone. This is not incompatible with the mechanism suggested.

The various facts concerning the photochemical decomposition of acetone and the fluorescence phenomena discussed above, indicate that the following reactions take place



It is possible that methyl radicals may react with acetone



(21) Kohlrausch and Pongratz, *Ber.*, **67B**, 976 (1934).

Direct dissociation instead of the formation of active molecules doubtless takes place in the continuum.

That the  $\text{CH}_3\text{CO}$  radical is relatively unstable is indicated by the almost total absence of biacetyl formation at 60°<sup>11</sup> and the fact that the photochemical decomposition of biacetyl at 100° gives almost solely ethane and carbon monoxide.<sup>22</sup>

Spence and Wild<sup>11</sup> find the ratio of ethane to carbon monoxide to increase with intensity when radiation in the continuum is absorbed by acetone, approaching a limiting value of 2.5. This is to be ascribed to the influence of reaction (27). In the full arc this ratio passes through a maximum and then decreases toward a limiting value of about 1.5. This would be due to (30), (31) and (29). In the banded region also the  $\text{C}_2\text{H}_6/\text{CO}$  ratio is nearly one, which would be ascribed to the high efficiency of (30) and the subsequent reactions (31) and (29). Thus biacetyl would have little chance of continued existence in the presence of excited acetone molecules.

While reactions (24) to (35) account for many of the experimental facts, the resulting kinetic expression would be so complex that it cannot be tested with data now available.

The effect of biacetyl formation is to tend to lower the ratio of slope to intercept in the previous work.<sup>10</sup> The calculated mean life for excited acetone would be, if anything, too small and, as concluded previously for other reasons, the value of  $4 \times 10^{-10}$  sec. is a lower limit.

In conclusion the authors wish to express their appreciation to Dr. C. F. Fisk, who built the Du-Bridge and Brown amplifier and made some preliminary runs on the work herein presented.

## Summary

1. An apparatus for studying the fluorescence of gases is described.
2. The ratio of absorbed to fluorescent intensity of acetone is a function both of incident intensity and of time of exposure. Only at very low intensities is a Stern-Volmer equation obeyed.
3. The fluorescence spectra of acetone and of biacetyl are identical at wave lengths longer than 5000 Å. The fluorescence in the blue, which alone appears when oxygen is present, is much weaker than the fluorescence at longer wave lengths and could not be photographed.

(22) Porter, Ramsperger and Steel, *THIS JOURNAL*, **45**, 1827 (1923).

4. Small amounts of biacetyl greatly increase the fluorescence of acetone.

5. It is concluded that the fluorescent emitters are the same for both acetone and biacetyl, at least as regards the bands at 5000 Å. and longer wave lengths.

6. Mechanisms to account for these facts are

advanced. An adequate explanation is based on a very probable deactivation of excited acetone molecules by biacetyl, the excited biacetyl being responsible for the fluorescence. However, fluorescence of the  $\text{CH}_3\text{CO}$  radical cannot be excluded.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## The Absorption Spectrum of Biacetyl between 1500 and 2000 Å.

BY VICTOR R. ELLS

In connection with work on the spectroscopy and photochemistry of ketones it was thought advisable to study the absorption spectrum of biacetyl. This substance is formed during the photochemical decomposition of acetone<sup>1</sup> and is a possible product, along with other diketones, during the irradiation of ethyl methyl ketone. Since absorption coefficients of the ketones below 2000 Å. are far higher than in the near ultraviolet, it was hoped that the absorption spectrum might be used to detect even small amounts of biacetyl.

As would be expected the juxtaposition of two chromophoric groups causes a displacement of the absorption spectrum toward longer wave lengths. Thus in the near ultraviolet biacetyl vapor absorbs to 4670 Å.,<sup>2</sup> whereas acetone<sup>3</sup> and ethyl methyl ketone<sup>4</sup> show absorption to only between 3200 and 3300 Å. Below these absorption regions both biacetyl and the other ketones show a broad zone of transmission extending to below 2000 Å., where an intense absorption takes place.

Biacetyl shows bands with fine structure from 4670 to 4400 Å. at which point the bands become diffuse. Continuous absorption is observed below 2800 Å.<sup>2</sup> and extending to about 2500 Å.

Lardy<sup>5</sup> and Lutly<sup>6</sup> have investigated the spectra of biacetyl and of glyoxal, respectively, in hexane solution. In biacetyl four bands occur between 4512 and 4054 Å., a wide band at 2800

and another at 1950 Å. being observed also. Glyoxal between 4613 and 3119 Å. shows seventeen bands and in addition there are bands at 2800 and 1950 Å. The substitution of a  $\text{CH}_3$  group for a hydrogen atom widens the narrow bands, reduces their number and increases the absorption coefficient.

### Experimental

The biacetyl (Eastman) was fractionated several times before being introduced into the storage bulb, after which it was again fractionated three times at low pressures in the vacuum line. Calcium chloride was used as a drying agent and the boiling point of the fraction taken was 87–88°. The freezing point was approximately –4°, although no value is recorded in the literature. No vapor pressure data could be found, but the observed vapor pressures were about 0.01 mm. at –70°, 1 mm. at –30° and 13 mm. at 0°.

A quartz cell with relatively thin windows was interposed between the hydrogen discharge tube and the slit of the vacuum spectrograph to avoid introducing the biacetyl directly into the spectrograph. Thus an absorbing column about 15 cm. in length and vapor pressures from 0.01 to 15 mm. were used. The spectrograph has been described.<sup>7</sup> Ilford I plates were used.

The dispersion of the spectrograph with the setting used was found to be 8.48 Å. per mm. in the first order. The 1931.027 Å. line of C III and a number of the fourth positive bands of carbon monoxide were used<sup>7</sup> as wave length standards. Since a quartz cell was employed, the lower limit of observation was about 1550 Å.

### Results

Twenty-six bands of biacetyl were found in all. These are listed in Table I, together with rough estimates of the intensities based on the pressure at which the bands appeared and their visually estimated intensities on the plates. The red edges of the bands appeared to be most sharp and are reported. Most of the bands were sufficiently

(1) Barak and Style, *Nature*, **135**, 307 (1935); Spence and Wild, *ibid.*, **138**, 206 (1936).

(2) Cf. Spöner, "Molekülspektren," Verlag von Julius Springer, Berlin, Vol. I, 1935, p. 117.

(3) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934). This paper contains references to earlier work. See also Noyes, *Trans. Faraday Soc.*, **33**, 1495 (1937).

(4) Duncan, Ells and Noyes, *THIS JOURNAL*, **58**, 1454 (1936).

(5) Lardy, *Compt. rend.*, **176**, 1548 (1923).

(6) Lothy, *ibid.*, **176**, (247 (1923)).

(7) *Read. Phys. Rep.*, **46**, 571 (1934).