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Photochemical Studies. XVIII The Fluorescence of Acetone Vapor

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A thorough understanding of the photochemical decomposition of acetone vapor must be accompanied by a study of the fluorescence of this substance. Previous work had indicated that the fluorescence is relatively weak, is affected by oxygen and (at least over part of the spectral range involved) possessed a fine structure. In the present work

it is shown that the intensity of the fluorescence follows the customary behavior observed in such phenomena in that it is quenched by the acetone vapor itself. A discussion is given as to the relationship of the fluorescence to the possible modes of photochemical decomposition.

THE fluorescence of acetone vapor has been observed by Damon and Daniels.¹ These authors state that the energy emitted in this way is a small fraction (perhaps much less than three percent) of the absorbed energy. Crone and Norrish² find that the fluorescence of acetone lies in the visible part of the spectrum and is diffuse. They interpret this as "predissociation in emission."

The possible interpretations of the photochemical decomposition of acetone vapor have been discussed by several authors.³ To summarize very briefly two mechanisms may be postulated: (1) after absorption of radiation carbon monoxide and ethane (the principal products) may be produced in one step by a unimolecular process; (2) free radicals may be formed, the course of the reaction being determined by the nature of the reaction chain.

Damon and Daniels¹ find that the quantum yield is low, increases at low intensities, decreases at low pressures and remains independent of wave-length between 3130 and 2650Å.⁴ The increase at low intensities favors the hypothesis of free radicals and the decrease at low pressures

indicates that the decomposition may not be unimolecular but of the type of predissociation by collisions.⁵

Norrish and Appleyard³ state that there is a sharp threshold of fluorescence near the beginning of the absorption spectrum and that in the region of diffuseness beyond 3000Å there is no trace of fluorescence even at low pressure. This fact would be difficult to reconcile with a quantum yield strictly independent of wave-length.

It is evident that a complete understanding of the photochemical decomposition of acetone vapor necessitates a thorough study of the fluorescence. The spectroscopic aspects of this phenomenon have been studied by others, so that we have confined ourselves to an investigation of the intensity of the fluorescence with varying experimental conditions.

A. EXPERIMENTAL PROCEDURE

As pointed out by Damon and Daniels³ the fluorescence of acetone vapor is weak and is markedly affected by the presence of oxygen, the color changing from green to blue when this substance is present.

As a source of exciting radiation a capillary mercury arc lamp similar to that described by Forbes and Harrison⁶ was employed. A crystal quartz prism and crystal quartz lenses, together with a suitable slit system were used to furnish monochromatic radiation of wave-length 3130Å. Since the quantitative formulation of the law

¹ G. H. Damon and F. Daniels, *J. Am. Chem. Soc.* **55**, 2363 (1933).

² H. G. Crone and R. G. W. Norrish, *Nature* **132**, 241 (1933). In a private communication Dr. Norrish has stated that the discrete ultraviolet fluorescence previously reported has not been confirmed.

³ See G. H. Damon and F. Daniels, reference 1; F. W. Kirkbride and R. G. W. Norrish, *Trans. Faraday Soc.* **27**, 407 (1931); R. G. W. Norrish, *ibid.* **30**, 103 (1934); R. G. W. Norrish and M. E. S. Appleyard, *J. Chem. Soc.* **1934**, 874; W. A. Noyes, Jr., *Rev. Mod. Phys.* **5**, 280 (1933).

⁴ See, however, R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J. Am. Chem. Soc.* **56**, 1644 (1934) who state that the yield is not strictly independent of wave-length.

⁵ See W. A. Noyes, Jr., reference 3.

⁶ G. S. Forbes and G. R. Harrison, *J. Am. Chem. Soc.* **47**, 2449 (1925).

governing the fluorescence necessitates highly monochromatic radiation, in some experiments color filters were employed in conjunction with the monochromator. For this purpose potassium chromate was usually employed, although Red Purple Correx glass was used in one experiment. By rough experimental test radiation of wavelengths other than those at 3130Å amounted to less than one percent of the total. Fluorescent screens were used for focussing the monochromator.

The intensity of the incident radiation was measured by a photoelectric cell (caesium-caesium oxide cell with quartz envelope) placed either directly back of the absorption cell or arranged so that it could be moved into a reproducible position in front of the absorption cell. The beam of incident radiation was diaphragmed in such a way that it was entirely intercepted by the photoelectric cell.

A T-shaped fluorescence cell was used, the incident radiation passing through the horizontal portion. Plane fused quartz windows were attached with picein wax. Below the lower limb at a distance of about 8.5 cm was placed a metal plate perforated by a hole 3 mm in diameter behind which could be placed a photographic plate protected by a shutter. A piece of plate glass was interposed to absorb scattered 3130Å radiation. The fluorescence falling in the spectral range from about 4000Å to the long wave limit of an Eastman 33 plate was studied.

Blanks were always made with no acetone in the cell to make sure that scattered radiation was unimportant. Corrections were always made for scattered radiation, but they amounted to less than experimental error.

The photographic plate was exposed to the fluorescent radiation for a specified length of time, five or six spots being made under varying conditions of pressure, incident intensity, etc. Subsequently spots were placed on the plate by radiation of known relative intensity. For this purpose a small hole illuminated by a 10 watt lamp protected by a Wratten green filter was used as a standard source and the inverse square law for intensities assumed. The spots due to the standard radiation were always placed near the spots made by the fluorescent radiation, although the uniformity of the emulsion was such that this

precaution was hardly necessary. The length of exposure of the fluorescence was always very nearly the same as for the standard.

The blackening of the spots was then measured by means of a photoelectric cell, by using a beam small compared to the diameter of the spot. By having several standard spots of varying degrees of darkening the interpolation did not extend over a wide range of intensity.

The acetone had been specially purified in the laboratory of Professor Kraus for solubility work. It was further purified by fractional distillation at low pressures.

The intensity of the fluorescent radiation has been studied as a function of the incident intensity, and the acetone pressure. Since oxygen affects the fluorescence, the acetone in the present experiments was thoroughly outgassed by evacuation with a mercury diffusion pump while condensed with liquid air. In appearance the fluorescence was always greenish.

B. RESULTS

In order to show how the results were calculated we will illustrate by means of one run given in detail.

The absorption coefficient for 3130Å radiation is 6.63 (concentration in moles per liter, distance in centimeters).⁷ The length of path from which radiation could be incident on the photographic plate is 2 cm (beginning 2 cm from the incident window) and the over-all length of the absorption cell is 6.5 cm.

The data of Table I were obtained in one run.

A plot is now constructed of $\log B/A$ vs. I_s . For the spots $\log B/A$ should be a numerical measure

TABLE I.

Pressure (cm)	5.2	8.6	10.8	14.9	18.9			
Galv. deflection (transmitted light)	2.05	1.89	1.73	1.57	1.45			
Absorbed in element 2 cm in length	0.0842	0.134	0.158	0.211	0.260			
Distance of standard (cm)	25	35	40	45	50	55	60	70
Deflection through spot (<i>A</i>)	2.50	4.50	5.75	7.30	8.50	9.40	9.95	10.50
Deflection through plate near spot (average) (<i>B</i>)	10.93	10.95	10.87	11.12	11.10	11.17	11.15	11.20
Intensity <i>I_s</i> (50 cm = 1)	4.00	2.04	1.56	1.23	1.00	0.827	0.695	0.510

⁷ Cf. reference 1; C. W. Porter and C. Iddings, J. Am. Chem. Soc. **48**, 40 (1926).

TABLE II.

Pressure (cm)	5.2	8.6	10.8	14.9	18.9
Deflection through spot (A_1)	9.95	9.45	9.20	8.55	7.90
Deflection through plate near spot (average) (B_1)	10.90	10.95	11.07	11.10	10.93

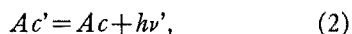
of the darkening. The data of Table II were obtained for the spots produced by the fluorescent radiation.

By comparing $\log B_1/A_1$ with the graph previously constructed the following relative intensities are obtained (the intensity of the standard radiation at 50 cm = 1)

Pressure (cm)	5.2	8.6	10.8	14.9	18.9
Relative intensity I_f	0.62	0.78	0.85	0.99	1.09

In those experiments in which the incident intensity was varied, various thicknesses of Pyrex glass or of cellophane were placed in front of the entrance slit of the monochromator. Otherwise the method was identical with that described above.

In presenting the results in detail it seems wise at first to give a possible elementary theory of the fluorescence. The mechanism may be represented by the following reactions:



If D_1 is the galvanometer deflection due to the radiation incident on the volume element from which the fluorescent radiation is to be studied then the incident intensity is

$$I_1 = k_1 D_1, \quad (4)$$

where k_1 is a proportionality constant necessary for converting deflection units into the desired units of intensity. The total radiation absorbed in the volume element will be

$$I_a = I_1 A (1 - \exp(-kcl)), \quad (5)$$

where A is the area of the beam and l is the length of the volume element. k is the absorption coefficient (6.63 as given above). The rate of formation of excited acetone molecules (in the entire volume element, not per unit volume) will be

$$+d(Ac')/dt = k_2 I_a = k_2 k_1 D_1 A (1 - \exp(-kcl)). \quad (6)$$

The rate of disappearance of excited acetone molecules will be

$$-d(Ac')/dt = k_3(Ac') + k_4(Ac')(Ac), \quad (7)$$

where (Ac') and (Ac) represent the numbers of excited and normal acetone molecules in the volume element (not per unit volume). Since the number of excited molecules is at any instant very small and since in the present experiments photochemical decomposition was never appreciable we may write

$$(Ac) = K_1 P, \quad (8)$$

where P is the total pressure of the acetone. By equating (6) and (7) (for the steady state) and substituting by Eq. (8) we obtain

$$(Ac') = k_1 k_2 D_1 A (1 - \exp(-kcl)) / (k_3 + k_4 K_1 P). \quad (9)$$

But the intensity of the fluorescent radiation will be

$$K_2 k_3 (Ac') = I_f = K_2 k_3 k_1 k_2 D_1 A (1 - \exp(-kcl)) / (k_3 + k_4 K_1 P), \quad (10)$$

where K_2 is a proportionality constant necessary for converting the number of acetone molecules in the volume element which lose their energy by fluorescence per second to the arbitrary units used for measuring the intensity of the fluorescence. Hence

$$D_1 (1 - \exp(-kcl)) / I_f = 1 / k_1 k_2 K_2 A + k_4 K_1 P / k_1 k_2 k_3 K_2 A. \quad (11)$$

It will be seen from Eq. (11) that if the simple mechanism given above for the fluorescence is adequate a plot of $D_1 (1 - \exp(-kcl)) / I_f$ vs. P should give a straight line. Fig. 1 shows two such plots for typical runs.

Since for a given run all of the quantities in Eq. (11) are constant except D_1 , I_f , c and P , it follows that the slope divided by the intercept is $k_4 K_1 / k_3$. k_3 is a first order constant and should depend only on the time units chosen. Since K_1 is a constant which relates pressure to the number of molecules in the volume element it will remain constant as long as the geometry of the system is unchanged. k_4 is the fraction of the excited acetone molecules deactivated per unit time per molecule of acetone present in the

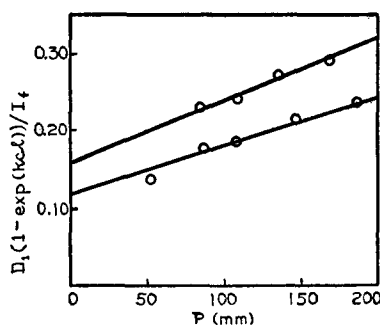


FIG. 1.

volume element. k_4K_1 is the fraction of the excited acetone molecules deactivated per unit time at unit pressure by collision. Both k_4K_1 and k_3 will be independent of the geometry of the system and the slope divided by the intercept should not change from one run to another even though the shape of the beam might vary somewhat.

Table III gives the data obtained during the last five runs obtained after most of the experimental difficulties had been removed.

TABLE III. Variation of fluorescence with pressure.

Pressure (cm)	7.1	10.2	13.7	16.6	18.9
$D_1(1 - \exp(-kcl))$	0.0314	0.0663	0.0868	0.101	0.110
I_f	1.72	1.82	2.07	2.28	2.45
Slope/intercept	0.053				
Pressure (cm)	5.4	9.7	12.9	15.8	17.9
$D_1(1 - \exp(-kcl))$	0.038	0.064	0.082	0.097	0.108
I_f	0.30	0.42	0.49	0.56	0.58
Slope/intercept	0.052				
Pressure (cm)	5.2	8.6	10.8	14.9	18.9
$D_1(1 - \exp(-kcl))$	0.084	0.1	0.158	0.210	0.260
I_f	0.62	0.78	0.85	0.99	1.09
Slope/intercept	0.054				
Pressure (cm)	3.3	6.7	10.1	18.2	18.4
$D_1(1 - \exp(-kcl))$	0.036	0.072	0.103	0.173	0.191
I_f	0.29	0.55	0.68	0.79	0.91
Slope/intercept	0.050				
Pressure (cm)	8.5	10.9	13.5	16.8	
$D_1(1 - \exp(-kcl))$	0.351	0.447	0.606	0.743	
I_f	1.54	1.86	2.24	2.57	
Slope/intercept	0.049				
Average slope/intercept 0.052					

Inspection of Eq. (11) shows that $D_1(1 - \exp(-kcl))$ plotted against I_f at constant pressure should give a straight line passing through the origin. Four runs were made at a pressure of 121 mm to test this point. A straight line plot was obtained in every case, although it did not quite pass through the origin in two of the four experiments. The actual ratios of $D_1(1 - \exp(-kcl))/I_f$ are given in Table IV.

TABLE IV. Variation of fluorescence with incident intensity.

$D_1(1 - \exp(-kcl)) (M)$	1.96	1.37	0.90	0.53
$D_1(1 - \exp(-kcl))/I_f (N)$	1.0	1.0	1.0	1.0
M	1.68	1.26	0.95	0.71
N	1.9	1.8	1.7	1.9
M	2.53	1.56	1.47	0.65
N	1.5	1.3	1.3	1.1
M	3.45	2.00	1.22	0.86
N	1.4	1.5	1.3	1.2
				1.0

C. DISCUSSION

To a first approximation Eq. (11) seems to agree with the experimental facts. The theory upon which this equation is based is obviously inadequate. At 25°C acetone molecules will exist in a variety of vibration and rotation energy levels and many levels must be formed by the absorption of radiation contained in the group of lines at 3130Å. A detailed statistical theory would be necessary for a rigorous explanation of the experimental facts. Unfortunately not enough information is available to permit such a study to be made, even if it were possible to carry out the necessary mathematical manipulations.

Let us examine a little more fully the conclusions which may be drawn from the simple theory upon which Eq. (11) is based and then point out the modifications which would be necessary for a more complete theory. The number of collisions per excited acetone molecule per second at a pressure of one centimeter is

$$Z_e = 4.78 \times 10^{22} \sigma^2 \quad (12)$$

at 25°C, where σ is the distance between centers at the time of "collision." If every collision is effective in deactivating an excited molecule, the rate of deactivation will be

$$-d(Ac')/dt = 4.78 \times 10^{22} \sigma^2 (Ac') P, \quad (13)$$

where P is the acetone pressure in centimeters. If J_a is the number of quanta absorbed per second in the volume element and J_f is the number of quanta emitted as fluorescence from the volume element per second we may write

$$J_a/J_f = 4.78 \times 10^{22} \sigma^2 P / k_3 + 1. \quad (14)$$

Eq. (14) is analogous to Eq. (11). Since the arbitrary units used in measuring the light

intensities cancel out in dividing the slope by the intercept in Table III, we may write

$$0.05 = 4.78 \times 10^{22} \sigma^2 / k_3. \quad (15)$$

The value of σ is not known, but may be taken as approximately 5×10^{-8} cm. This gives $k_3 = 2.4 \times 10^9$ sec.⁻¹ and the mean life of the excited acetone molecule would be 4×10^{-10} sec. It is true that by introducing an efficiency factor for collisions into Eq. (12) or by reducing the value of σ one can cause an increase in the value obtained for the mean life, without, however, changing in any essential respect the considerations in the following paragraphs. 4×10^{-10} sec. may be considered as a minimum figure.

From the figures given in the preceding paragraph one can calculate the fraction of the absorbed energy which should be reemitted in the form of fluorescence at a pressure of 250 mm, where Damon and Daniels¹ observed this fraction to be less than 0.03. Calculation shows that the number of emitted quanta should be about 45 percent of the number of absorbed quanta.

The discrepancy between the observed and calculated values is beyond the limits of experimental error and necessitates a modification of the theory. One might assume, for example, that a series of upper states are formed each with its own specific rates of fluorescence and deactivation. Each of the members on the right side of Eq. (7) would then be replaced by a summation. The problem would be hopelessly complex unless it is assumed that the relative rates of formation of the molecules in the various states remain independent of pressure. A superficial examination will indicate, however, that this method of approach will not resolve the difficulty made apparent in the preceding paragraph.

One other obvious method of approach suggests itself in that Eqs. (1), (2) and (3) take no account at all of the photochemical decomposition. This decomposition may result either by a first order step or by a second order step involving predissociation by collision. The photochemical evidence is not unambiguous on this point. However since Eq. (11) seems to account satisfactorily for the fluorescence data, the

introduction of the photochemical decomposition must not alter the form of this equation and yet it must provide a mechanism whereby the amount of fluorescence will be decreased. This can be done by introducing a fourth step

$$Ac' = D, \quad (16)$$

where D represents dissociation products. Let the specific rate constant for this reaction be k_4 . It can now be shown that the slope divided by the intercept will be $k_4 K_1 / (k_3 + k_4)$. Thus $(k_3 + k_4) = 2.4 \times 10^9$. By using a value of the quantum yield one can now calculate an upper limit to the fraction of the absorbed radiation which should appear as fluorescence. If the quantum yield is taken as 0.3, the maximum fraction of the incident quanta which could appear as fluorescence is 0.14. (Since the wave-length of the fluorescence radiation is longer than that of the incident radiation, the fraction of the *energy* re-emitted would be between 0.07 and 0.10.) There is the further possibility, as suggested by Norrish and his co-workers,⁴ that some internal rearrangement may take place unaccompanied by either fluorescence or decomposition.

In conclusion it should be emphasized that this mechanism will not account for a decrease in quantum yields at low pressures. Indeed by including a short chain reaction or by introducing predissociation by collisions to account for a *small* fraction of the photochemical decomposition the above results would not be seriously modified. The slight decrease in yield at high intensities¹ argues strongly for the existence of reaction chains.⁸

There seems to be some disagreement among various workers as to whether fluorescence is of equal importance for all incident wave-lengths.⁹

The authors wish to express their appreciation for a grant-in-aid obtained from the National Research Council which aided materially in pursuing this and related investigations.

⁸ See J. A. Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934) for a discussion of the very analogous case of acetaldehyde in which two types of decomposition seem to take place at room temperature.

⁹ Cf. reference 1; R. G. W. Norrish, Nature **133**, 837 (1934).