[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXIX. A Further Study of the Fluorescence of Acetone

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The problem of energy exchange between polyatomic molecules is one about which relatively little is known experimentally and for which the theory can be stated only in general, and somewhat unsatisfactory, terms. There is, perhaps, no more fundamental problem in the field of reaction kinetics, and studies of fluorescence offer one means of obtaining data essential to a more satisfactory statement of the theory. Interpretations of this type of data are difficult and are usually based on classical assumptions which do not add materially to the field.

Studies of the fluorescences of acetone and of biacetyl have been numerous and yet there are still many points of ambiguity. The present study was started with a view to obtaining a better insight into the behavior of these fluorescences. While certain points have been clarified, much remains to be done before a final understanding of all of the data will be possible.

Summary of Previous Work

The fluorescence of acetone vapor seems to have been described first by Damon and Daniels[3] who observed both green and blue parts, the former at least six times as intense as the latter. Damon[4] and Fugassi[5] extended the study to acetone–oxygen mixtures, the change in visual color from blue to green being an indication of the disappearance of oxygen. Fugassi[5] showed the quantum yield of oxygen disappearance to be equal to that of acetone disappearance in an oxygen-free system.

The existence of fluorescence might normally indicate a discrete absorption spectrum. Such an absorption was found by Norrish, Crone and Saltmarsh[6] and further studied by other authors.[7] However, the existence of a threshold[8] for exciting the fluorescence has not been confirmed, and it is now generally agreed that acetone fluoresces at both 3130 Å. and 2537 Å. although more weakly at the latter wave length. A complete description of the absorption spectrum is not possible at the present time. There may be a continuum underlying the whole absorption region from about 2400 Å. to about 3200 Å. The bands may have a diffuse character, indicating the possibility of predissociation, but with a complex molecule of this type any definite conclusions in this connection are unwarranted. In any case there seems to be no fundamental difference (other than magnitude of certain quantum yields) between the photochemical behaviors of acetone at 3130 Å. and at 2537 Å.[9] Acetone shows many sharp bands in the region below 2000 Å.,[10] but no fluorescence could be observed by excitation with wave lengths between 1800 and 2000 Å.[11]

The first attempt at a quantitative study of the fluorescence of acetone with 3130 Å. radiation showed that plots of I_a/I_f *vs.* pressure gave reasonably straight lines (I_a = intensity loss due to absorption of radiation, I_f = intensity of fluorescence.)[12] Due to the experimental method long exposures were used, and while the total fluorescence (green plus blue) was measured, the major portion of the fluorescence was undoubtedly in the green.[3] Moreover, only relatively high pressures (over 30 mm.) could be studied and the true effect of collisions could not be ascertained. An attempt to repeat this work[13] by a different method indicated that the fluorescent intensity was a function of time. The green parts of the fluorescences of biacetyl and of acetone were shown to be identical. This led Matheson and Zabor[14] to examine the fluorescences of other compounds containing the CH_3CO- group, thus showing the same fluorescence to be found in acetaldehyde and methyl ethyl ketone. The emitter seems to be the same (for the green) for all of these compounds and is probably biacetyl.

The most precise work on the fluorescences of acetone and of biacetyl is due to Almy and his co-

(1) National Research Council Predoctoral Fellow, December, 1945 to April, 1947.

(2) This work was supported in part under Contract N6onr-241, Task I, with the United States Navy.

(3) G. H. Damon and F. Daniels, THIS JOURNAL, **55**, 2363 (1933).

(4) G. H. Damon, *Ind. Eng. Chem., Anal. Ed.*, **7**, 133 (1935).

(5) P. Fugassi, THIS JOURNAL, **59**, 2092 (1937).

(6) R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

(7) W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.*, **2**, 717 (1934); W. A. Noyes, Jr., *Trans. Faraday Soc.*, **33**, 1495 (1937).

(8) R. G. W. Norrish and M. Appleyard, *J. Chem. Soc.*, 874 (1934).

(9) A disagreement is indicated from the ratios of ethane to carbon monoxide found by R. Spence and W. Wild, *J. Chem. Soc.*, 352 (1937); 590 (1941), and by D. S. Herr and W. A. Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940), respectively. The ratios obtained by the former authors would indicate little or no biacetyl to be formed at 3130 Å. The probable explanation of this discrepancy is found in the work of Damon and Daniels[3] and of G. M. Almy and S. Anderson, *J. Chem. Phys.*, **8**, 813 (1940), which showed that biacetyl (probably mistaken for diacetone alcohol by Damon and Daniels) does not accumulate indefinitely in the system, particularly when polychromatic light is used. The work of J. G. Roof and F. E. Blacet, THIS JOURNAL, **63**, 1126 (1941), showed that the photochemical decomposition of biacetyl is a chain reaction under some conditions and the reaction should be initiated, therefore, by free radicals from acetone. For a review, see W. Davis, Jr., *Chem. Rev.*, **40**, 201 (1947).

(10) See W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, ref. 7.

(11) J. P. Howe and W. A. Noyes, Jr., THIS JOURNAL, **58**, 1404 (1936).

(12) C. F. Fisk and W. A. Noyes, Jr., *J. Chem. Phys.*, **2**, 654 (1934).

(13) M. S. Matheson and W. A. Noyes, Jr., THIS JOURNAL, **60**, 1862 (1938).

(14) M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 536 (1939).

workers.[15] This work confirms and extends earlier work. The main conclusions from all work thus far may be summarized briefly as follows: (1) The green fluorescence is associated with the presence of biacetyl and the biacetyl molecule is probably the emitter.[13,14,15] (2) The weak blue fluorescence is found in carefully purified acetone and also in acetone with oxygen present and is probably due to the acetone molecule.[3,4,5,15,19] (3) The quantum yield of fluorescence is low for both acetone and biacetyl, not over 2 or 3% in the most favorable case in acetone and probably much less for the blue alone; in biacetyl an efficiency of 14 per cent. is found.[15] (4) The lifetime of the excited state in biacetyl is quite long, of the order of 1.5×10^{-3} sec.[15,16] (5) At temperatures over about 100° there is very little green fluorescence,[14] indicating that biacetyl is not produced from acetone at such temperatures.[17] (6) Either the emission process in biacetyl is not the direct reverse of the absorption process or only a small fraction of the absorbing molecules reach the state which can fluoresce. Lewis and Kasha[18] designate the upper state as triplet and describe the fluorescence as phosphorescence due to the long life. (7) While the fluorescences of biacetyl excited by 4358 Å. and 4047 Å. are normal in the sense that they are quenched by collisions,[15] that excited by 3660 Å. shows the reverse effect.[19,15] This can be explained by assuming that molecules excited by 3660 Å. are capable of dissociating unless stabilized by collisions, whereas those produced by the other two wave lengths are not. (8) As acetone is irradiated, the blue fluorescence grows weaker as the green grows stronger.[15] (9) The green fluorescence reaches nearly full intensity when the biacetyl pressure is very low[13,19,15] (not over a few tenths of a millimeter) compared to the acetone pressure (100 mm. or more), thus indicating some mechanism which is quite specific and which is not inhibited markedly by the acetone. (10) Experiments with deutero-biacetyl indicate that there is probably little reaction of the type $CH_3 + CD_3COCOCD_3 = CH_3COCD_3 + COCD_3$[20] at temperatures up to 62°. (11) The blue fluorescence is observed in solid acetone and possibly also in other solid ketones.[21]

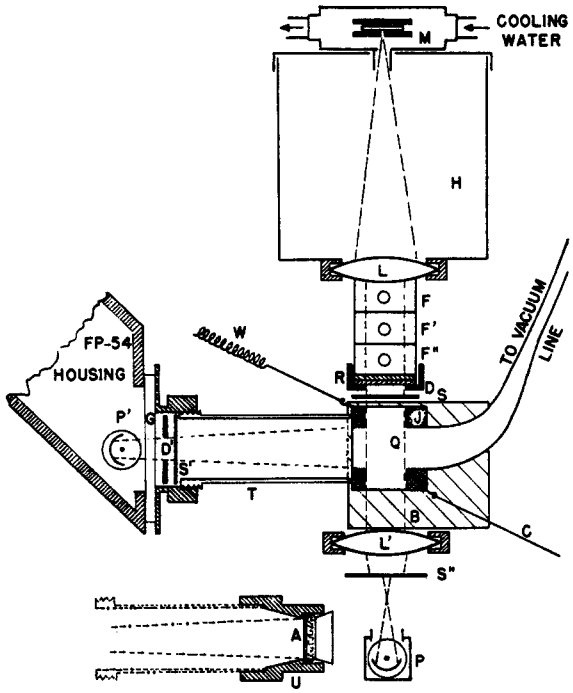


Fig. 1.—Diagram of optical set-up, including fluorescence cell, light source and filters, and transmission and fluorescence photocells: A, radium-activated phosphor disc; B, bench on which cell can move; C, cord removing cell from beam; D,D′, diaphragms; F,F′,F″, filter solutions; G, glass filter, Corning no. 738; H, housing to enclose light; J, jacket of copper around cell; L,L′, lenses (quartz 14-cm. focus); M, mercury arc (H-6 shown); P,P′, photocells, GL-929; Q, quartz fluorescence T-cell; R, red-purple Corex glass filter; S,S′,S″, shutters; T, tube for constant light path; U, unit for calibrating fluorescence photocell circuit; W, wire spring to return cell.

From the above it may be stated that two points, among others, need clarification: (a) the mechanism of excitation of the fluorescence ascribed to biacetyl when acetone is the absorbing molecule; (b) the relationship of the blue fluorescence to the green. The present work was performed with the object of clarifying some of the steps in the mechanism of these fluorescences.

Experimental

The acetone (J. T. Baker C. P.) was fractionally distilled after standing for two days in the dark over anhydrous calcium chloride. The middle half was collected and the distillation repeated. The middle half from this second distillation was stored under vacuum over anhydrous calcium sulfate and fractionally distilled from a temperature of 0° to one of −7°. The middle half from this final step, amounting to about 4 cc., was kept in a blackened storage reservoir separated from the line by a mercury cut-off.

Oxygen was prepared by heating C. P. potassium permanganate, passed through glass wool and a trap immersed in liquid nitrogen. It was stored in a one-liter bulb separated from the line by a mercury cut-off.

For most of the experiments a General Electric AH-6 high pressure mercury arc was used. The optical system, including the color filters, is shown schematically in Fig. 1. The color filter combination consisted of a 5-cm. length of 0.0005 *m* potassium chromate, 5 cm. of 0.356 *m* nickel chloride, and 1.0 cm. of 0.0245 *m* potassium biphthalate. The emission lines from this type of arc are

(15) G. M. Almy, H. Q. Fuller and G. D. Kinzer, *J. Chem. Phys.*, **8**, 37 (1940); G. M. Almy and S. Anderson, *ibid.*, **8**, 805 (1940); H. Q. Fuller, L. W. Phillips and G. M. Almy, *ibid.*, **7**, 973 (1939); G. M. Almy and P. R. Gillette, *ibid.*, **11**, 188 (1943).

(16) R. D. Rawcliffe, *Phys. Rev.*, **59**, 915 (1941).

(17) See D. S. Herr and W. A. Noyes, Jr., ref. 9.

(18) G. N. Lewis and M. Kasha, THIS JOURNAL, **67**, 1001 (1945).

(19) F. C. Henriques, Jr., and W. A. Noyes, Jr., *ibid.*, **62**, 1038 (1940).

(20) D. S. Herr, M. S. Matheson and W. D. Walters, *ibid.*, **63**, 1464 (1941).

(21) Unpublished results kindly shown to us by Dr. A. B. F. Duncan of this Laboratory.

very broad, and hence the radiation is not strictly monochromatic, although at least 95% lies in the region of 3075–3250 Å.[21a]

A Hanovia 150-watt Uviarc was used for part of the work. This arc operates at a much lower pressure than the AH-6 and with the color filter combination at least 95% of the radiation lay in the group of lines at 3130 Å.

The beam incident on the fluorescence cell was parallel and practically homogeneous. It filled 90% of the transmission arm with little or no radiation hitting the walls. Scattered radiation reaching the photoelectric cell used to measure the fluorescent intensity amounted to less than 0.1% of the fluorescent intensity in most cases. Even in the most unfavorable case (determination of the fluorescence at very low pressures) scattered radiation was not over 20% of the total.

Incident intensity was varied by means of fine mesh screens oxidized in a flame and used singly or in pairs. The meshes varied from 20 to 150 per inch with transmissions from 30 to 60%. The intensity was calculated from the measured transmissions of the screens in each case.[22]

The fluorescence cell, which had the form indicated in Fig. 1, was made of fused quartz with windows about 1.5 mm. in thickness. All portions of the cell except the windows were painted black. It was attached to the rest of the vacuum system by 6 feet of 8 mm. tubing, thus permitting it to be moved into and out of the light beam. For experiments at higher temperatures the cell was enclosed in a copper block cut in two sections and surrounded with a layer of asbestos, a winding of resistance wire and a second layer of asbestos. Temperatures were measured with a thermocouple inserted in a well drilled in the copper block.

Transmitted radiation was condensed with a quartz lens on a GL-929 photocell with a S-4 surface and the current measured with a galvanometer using an Ayrton shunt to vary the sensitivity.[23]

The fluorescent radiation was measured with a GL-929 photocell and d. c. amplifier employing an FP-54 electrometer tube and a modified DuBridge circuit.[24] The stability of the circuit was excellent except in very humid weather. The fluorescent radiation passed through a Corning glass filter no. 738, 2 mm. in thickness, which removed more than 99% of the ultraviolet radiation incident upon it.

The fluorescence amplifier circuit was calibrated by applying a fixed voltage to the control grid of the FP-54 tube and recording the resulting scale deflection. A one inch radium activated phosphor disc, emitting blue radiation at a brightness of 0.25 microlambert, was used as an absolute source of calibration.[25]

The circuit for measuring the transmitted intensity was calibrated with a small automobile light operating at exactly 5.55 volts from a storage battery. This circuit was checked before and after (and occasionally during) each run. This was necessary because of the extreme sensitivity of the galvanometer used. The reproducibility of the sensitivity left something to be desired.

At low acetone pressures the largest error lies in the experimental determination of the absorption by the acetone since this is determined as the small difference in two large quantities. Neither the constancy of the light source nor the constancy of the galvanometer sensitivity were adequate for this purpose. Especially after the accumulation of photochemical decomposition products and after the addition of other gases such as oxygen, the complete removal of the acetone by condensation with liquid air through the long tubing connecting the cell with the trap proved to be slow and unreliable. Hence, the procedure was adopted of removing the cell from the light path and determining the intensity of the beam directly. This coupled with a determination of the mean transmission of the two windows of the cell permitted a calculation of the intensity incident on the ketone if it is assumed that the two windows absorb and reflect to equal extents. The assumption of Beer's law for these very low absorptions is valid even if the light is not strictly monochromatic.

The procedure used may be described in the following steps: (1) measurements were made of I_t^0, I_0, and again of I_t^0 where I_t^0 is the light transmitted by the cell when the ketone is condensed by liquid nitrogen (but foreign gas, if any, is present) and I_0 is the intensity of the beam when the cell is removed from the light path; (2) the measurement of I_s^0, *i. e.*, the intensity of the scattered light; (3) remeasurement of I_0 and I_t^0 and a check of the zero reading of the transmission photocell with the shutter at S″ (Fig. 1) closed; (4) vaporization of the ketone into the cell, measurement of I_0, I_t (the light transmitted by the filled cell), and again of I_0; (5) measurement of I_f (the intensity of the fluorescence) and of I_t; (6) remeasurement of I_0 and I_t and a recheck of the zero readings of the transmission and fluorescent photocell circuits; (7) repetition of the empty cell readings after freezing down or pumping out the ketone.

The value of T (the fraction of total radiation transmitted through the first window) was obtained from an average of the empty cell readings before and after each run. Corrections were applied on the basis of calibrations made each day and for changes in shunt readings. The value of I_a was obtained from a corrected value of I_t. Dividing I_f and I_t by I_0 corrected for small changes in lamp intensity.

The value of $1/Q$ used in this article is the ratio I_a/I_f, where I_a is the actual loss in intensity in passing through the absorbing gas expressed in arbitrary units, where each unit is 1.6×10^9 quanta/second/cc. and I_f is the intensity of the fluorescence in arbitrary units.

The line for handling the gases and measuring pressures need not be described in detail. No stopcocks using grease were present in the line. Low pressures of gases not condensed by liquid nitrogen were measured with the McLeod gage. Foreign gases, such as oxygen, could be admitted from storage bulbs by the use of a Toepler pump. Pressures of the ketone were read directly on a manometer. The main disadvantage in the entire system resided in the long tubing between the cell and the trap, made necessary by the need of moving the cell into and out of the light path. This resulted in slow condensation of the ketone in the presence of non-condensable gases and also in slowness of diffusion back into the cell of biacetyl. The latter would vaporize more slowly than acetone after condensation by liquid nitrogen.

The transmitted light was photographed with a small Bausch and Lomb Littrow-type spectrograph and the fluorescence was photographed with a wide aperture glass prism spectrograph. Eastman I-F and I-G plates were used. Due to the low intensity of the fluorescence, particularly in the blue, a wide slit was necessary, thus render-

(21a) W. Davis, Jr. and R. E. Hunt, THIS JOURNAL, **69**, 1415 (1947).

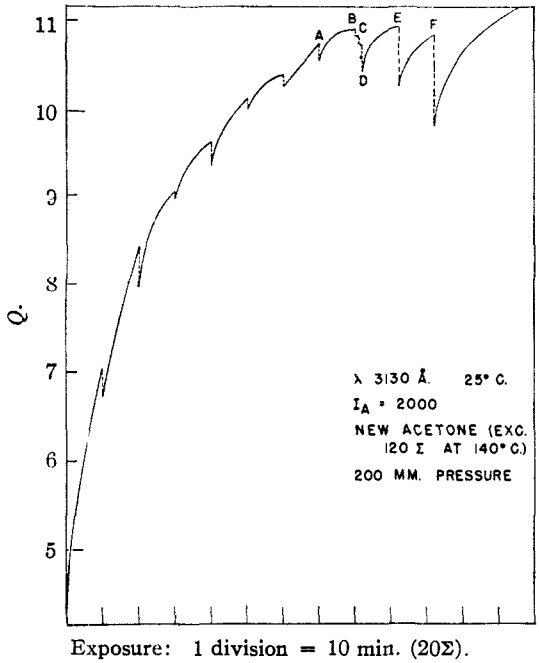
(22) The validity of varying light intensity in this way has been discussed by R. G. Dickinson (see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," The Reinhold Publishing Company, New York, 1941, p. 202.) The screens were placed just in front of the window through which radiation was incident on the ketone. This method reduces the total radiation but does not decrease the intensity per unit area for the portions illuminated. Other methods which might have been used to vary the light intensity would not have been valid unless the radiation were highly monochromatic. Comparison of results with the Uviarc and the AH-6 arc, while not extensive enough to warrant definite conclusions, did not show any striking differences in behavior. The latter arc was about 25 times as intense as the former.

(23) The light intensities absorbed by the ketones in the fluorescence cell were calculated from the values of the intensities of the transmitted light using the method of R. E. Hunt and T. L. Hill, *J. Chem. Phys.*, **15**, 111 (1947).

(24) The d. c. amplifier was designed and constructed by Dr. J. B. Platt of the Department of Physics and loaned for this work by Prof. Brian O'Brien of the Institute of Optics, University of Rochester.

(25) The disc was obtained from the United States Radium Corporation, which also furnished the brightness calibration. The brightness of this disc was of the same order of magnitude as that of the blue fluorescence.

ing uncertain any conclusions about the discrete character of the fluorescence. Microphotometer tracings were obtained in the recording microphotometer in the Institute of Optics.



Exposure: 1 division = 10 min. (20Σ).

Fig. 2.—Variation of total fluorescent efficiency (Q) with exposure as a function of intermittent dark periods. Unlettered breaks in curve are 5-min. dark periods; points A-C, 10-min. periods; D, 40 min.; E, 240 min.; F, 2 days.

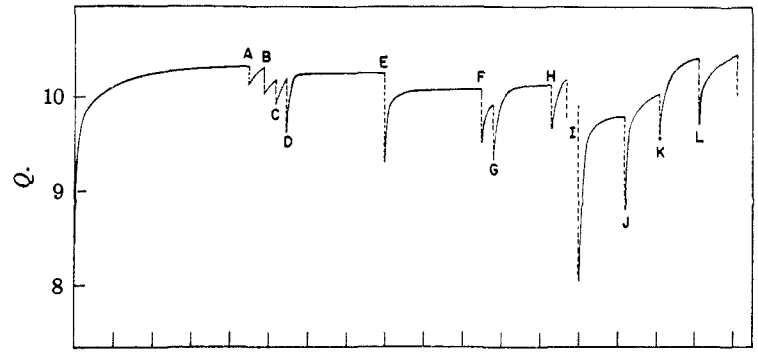
Discussion of Results

The trend of $1/Q$ (or of Q) as a function of several variables is more important than actual numerical values, and hence the results are presented graphically in Figs. 2–9, inclusive. The variables employed were absorbed intensity at constant pressure, pressure at constant absorbed intensity, and temperature.

At the start of a run with carefully purified acetone, the green fluorescence is weak or entirely absent but increases with time quite rapidly at room temperature. The blue fluorescence simultaneously decreases. Therefore, the radiation measured by the photoelectric cell consists mainly of green after the first few minutes except at elevated temperatures. Determination of the behavior of the blue as a function of various variables was accomplished satisfactorily only at temperatures above about 120° where the green was absent. Oxygen may eliminate the green entirely, but it also strongly decreases the intensity of the blue. At 0.4 mm. pressure of oxygen the green was absent and the blue decreased by a factor of ten.

Figures 2 and 3 indicate some of the reasons for difficulties in reproducing results. In Fig. 2 the quantity of Q (defined as the ratio I_f/I_a where I_f is the intensity of the fluorescence and I_a is the decrease in intensity due to absorption by the vapor) is shown as a function of time. Since these measurements were made with a photoelectric cell, they include both the green and the blue, although the green is at least three-quarters of the total intensity after the curve has ceased its rapid rise. The breaks in the curve are brought about by various dark periods as indicated in the caption. The decrease in Q after a dark period may be due either to a slow diffusion of some substance, presumably biacetyl, from the fluorescence cell into the rest of the apparatus or to a disappearance of this substance either due to a chemical reaction or perhaps due to polymerization. That it invariably occurred even after long periods of illumination would indicate that it is not entirely due to diffusion because eventually biacetyl would be expected to attain a more or less uniform concentration throughout the entire system. Earlier work[26] has given some indication of removal of biacetyl from the gas phase by a process which does not depend on illumination.

In Fig. 3 somewhat similar data are shown except that the acetone at the beginning of the curve had already been exposed to radiation for an appreciable length of time. Although in this instance the curves had reached approximate constancy during illumination, the value of Q was always found to be low after a dark period. The



Exposure: 1 division = 10 min. (20 Σ).

Fig. 3.—Variation of total fluorescent efficiency (Q) with exposure as a function of dark period duration and liquid nitrogen cooling: acetone sample had been used for two weeks under wide variety of conditions of intensity and temperature; pressure 163.7 mm.; temperature 24°; wave length 3130 Å.; I_a = 2000. Points A-E are dark periods of 5, 10, 20, 40, 80 min.; F-H, periods of 40, 40, 80 min. At point I, ketone was cooled with liquid nitrogen to −196° for 10 min., 20 mm. remaining unfrozen in the line due to slow diffusion through non-condensable products. After vapor had warmed to room temperature, fluorescence readings were begun at once. At J, after 10 min. at −196°, vapor stood 45 min. at 24° before readings were begun; at K, only 4.5 min. was allowed for diffusion. At L, liquid nitrogen was kept on ketone trap 3 min. only, with 4.5 min. allowed subsequently for diffusion.

(26) Unpublished results obtained by Dr. V. R. Ells.

effect of freezing out the acetone and any condensible reaction products with liquid nitrogen for varying periods of time is shown by points I, J, K and L. In this instance the lower rate of evaporation of biacetyl as compared to acetone almost certainly leads to a temporary deficiency of biacetyl in the fluorescent cell and Q is low until the concentration of this compound has been replenished through irradiation.

It has been shown[13] that the amount of biacetyl does not determine the intensity of the fluorescence providing it has reached a certain value, probably not over a fraction of a millimeter. There are also indications[15] that biacetyl reaches a steady state when acetone is illuminated. Data on this point are difficult to obtain and especially since it is not known whether the steady state concentration, if there is one, is the same when approached from both directions. The only clue to this point would be obtained from the data of Roof and Blacet[9] which indicate that under some conditions the photochemical decomposition of biacetyl is a chain reaction. It might, therefore, be initiated by free radicals from acetone.

The data in Figs. 2 and 3 do indicate, however, that Q for total fluorescence attains an approximately constant value after long periods of illumination. The blue intensity goes down about 50% during the period when the green builds up to its maximum. This is in agreement with the work of Almy and Anderson.[15]

The so-called green fluorescence consists of several "bands" whose wave lengths have been measured by other authors.[6,13,14,27] The blue fluorescence extends from about 3850 Å. to about 5000 Å. This fluorescence has one weak maximum which occurs near the long wave end of this region (see Fig. 4). This weak maximum may possibly be associated with the so-called green bands commonly ascribed to biacetyl. Evidence for this is uncertain, but the separation in wave numbers between the various maxima indicate that this conclusion has some merit. If the fluorescence due to the biacetyl occurs mainly from low vibration levels in an upper electronic state,[28] the transition corresponding to the maximum around 4650 Å. would have to be either to a lower vibration level in the ground state or from a higher vibration level of the upper state than the transitions ascribed to the other bands.

The effect of temperature on the green and blue fluorescences is indicated in Fig. 5. It is to be noted that the intensity of the green fluorescence decreases markedly with increase in temperature whereas the blue shows only a very gradual change and its value at 200° is still 20% of its value at 25°. The fact that the curve obtained with decreasing temperature lies lower than the curve obtained as the temperature increases may indicate a small decomposition of biacetyl at high temperature. This must be due to a photochemical reaction (perhaps with a high quantum yield) rather than a pure thermal reaction. On the other hand, even when biacetyl is known to be present the green is absent at temperatures of about 125° and above. Thus the increase in temperature has two effects: (1) it prevents formation of biacetyl, probably due to the instability of the acetyl radical and (2) it inhibits in some way the mechanism for exciting the green fluorescence.

Figures 6 and 7 show the effect of absorbed intensity on the fluorescence. In Fig. 6 the total fluorescence, blue plus green, is shown as a function of intensity, the intensity being varied by a

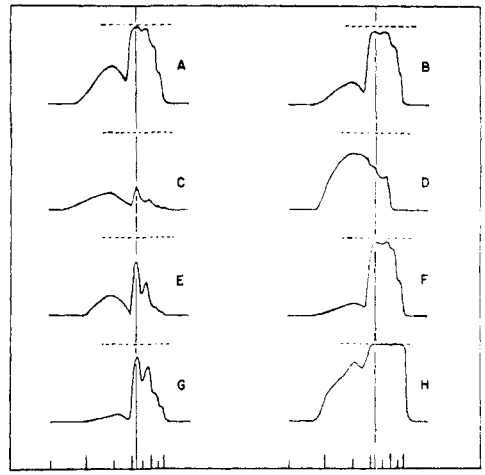


Fig. 4.—Representative microdensitometer tracings showing spectral distribution of acetone fluorescence under various conditions of excitation and exposure. Eastman I-F plates were used sensitized to 7000 Å. except for curve D for an I-G plate with the limit of 5800 Å. was used. A small glass spectrograph with 0.9 mm. slit was used. Acetone at a pressure of 170 mm. was irradiated by monochromatic 3130 Å. ultraviolet light except for curve H (see below). Exposure times with ten minutes except C and D. A New acetone 25°, irradiated 21 minutes, integrated intensity 90 Arbitrary Units. B. Same as A except time of irradiation 128 minutes, integrated intensity 550 Arbitrary Units. C. Old acetone irradiated at 120° with an integrated intensity of 820 Arbitrary Units plus irradiation at 25° for 1600 Arbitrary Units (30 min. exposure.) D. Solid acetone at −196°. Identical curve obtained after two hours of irradiation (5 min. exposure). E. Old acetone previously irradiated for 1200 Arbitrary Units at 25°, 0.01 to 0.04 mm. oxygen initially present. F. Old acetone previously irradiated for 2300 Arbitrary Units at 2500–3600 Å. at 25°, after which products non-condensable with liquid nitrogen were removed. Identical curve after 74 minutes additional irradiation. G. Old acetone exposed over a period of several minutes at 25°, slit width 0.5 mm. H. Old acetone irradiated at 2500–3600 Å. with two day intermediate dark period prior to photographing fluorescence. Exposure taken during irradiation with 2500–3600 Å.

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

(28) W. A. Noyes, Jr., and F. C. Henriques, Jr., *J. Chem. Phys.*, **7**, 767 (1939).

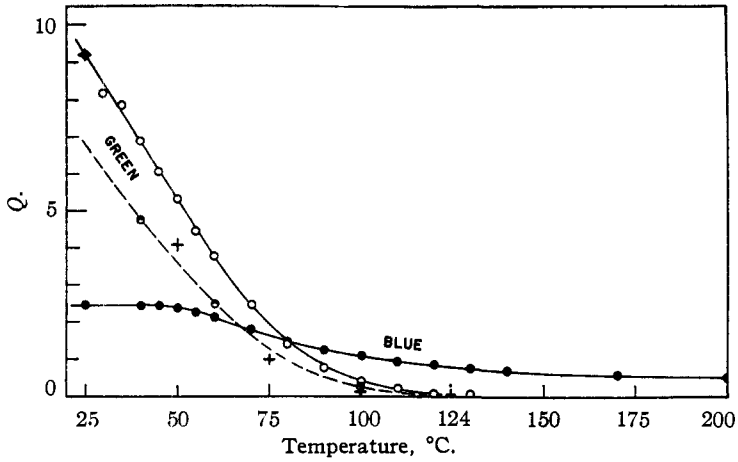


Fig. 5.—Fluorescent efficiency ($I_f/I_a = Q$) as a function of temperature for blue and green acetone fluorescence: pressure 165 mm.; wave length 3130 Å.: ●, blue, obtained spectrographically 25–140°, photometrically 140–200° (not corrected for varying spectral sensitivity of photocell)*; temperature increasing between points. O, green, obtained photometrically, correcting total deflections for presence of blue; increasing temperatures. ⊖, green, same; decreasing temperatures. +, green, obtained spectrographically; increasing temperatures.

factor of about 50. This particular sample had previously been exposed for some minutes at room temperature, part of the time with oxygen present. The variation with intensity is so slight as to be well within experimental error. In Fig. 7 the curve labeled "green" is obtained at room temperature and is really total fluorescence, mainly "green." Again there is no variation in intensity greater than experimental error. The measurements of the blue in Fig. 7 were made at 145° where the green is absent, and show at most an extremely small variation with intensity, certainly not much larger than experimental error.

In Figs. 8 and 9, $1/Q$ is shown as a function of pressure. In this instance the data are not so reliable as might be desired due to the difficulties of measuring percentage absorption at low pressures. It is believed that the values for the blue fluorescence in Fig. 8 for which the absorbed intensity is calculated from Beer's law at low pressures are most reliable.

$1/Q$ for the green, in contrast to the blue, shows some tendency to increase at low pressures. The curve in Fig. 9 is for total fluorescence; correction for the presence of the blue would cause a somewhat greater rise for the green alone at low pressures.

The detailed mechanisms for the blue and the green fluorescences can be discussed only in general terms. The interpretations given by Almy and his co-workers[15] are supported in broad outline, although some differences seem to be necessary.

A Stern–Volmer mechanism is not obeyed for either the blue or the green, although $1/Q$ *vs.* pressure at high pressures is a straight line in agreement with earlier data.[12] The relative insensitivity of $1/Q$ to large changes in pressure when the pressure is above about 50 mm. may indicate one of two things: (1) the molecule or radical responsible for the fluorescence has such an extremely short life in the activated state that it does not have time to be deactivated; or (2) the molecule or radical is extremely insensitive to collisions with acetone molecules. With the former assumption lifetimes perhaps as short as 10^{-8} second would be required, whereas Almy has shown that the lifetime of the active molecule responsible for the green is about 10^{-3} second.

A better estimate of the probable lifetime of the species responsible for blue emission can be obtained from the effect of oxygen which, as already stated, decreases the intensity of the blue when it is present at a pressure of 0.1 mm. Using the assumption that collisions of excited molecules with acetone have no effect and that collisions with oxygen are 100% efficient, one calculates a mean life for the excited species of about 10^{-5} second. This may be considered to be a lower limit. If the mechanism proposed by Almy and co-workers[15] whereby the biacetyl molecules are excited by collision of the second kind with excited ace-

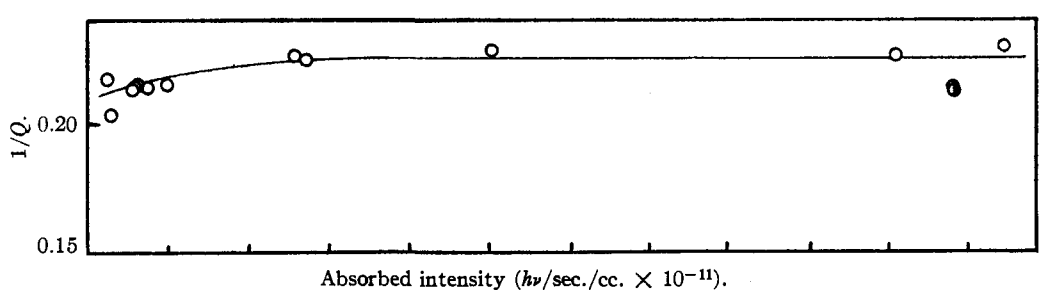


Fig. 6.—Quenching of total acetone fluorescence as a function of (low) absorbed intensity at constant pressure and temperature; sample pre-exposed 30Σ (8Σ with O_2); uviarc, λ3130 Å. 29°; pressure, 208 mm.: O, at decreasing intensity (adding resistance in circuit to cool arc); ◑, following day with hot arc.

* Corrected quantum efficiencies of blue are about half that shown on graph.

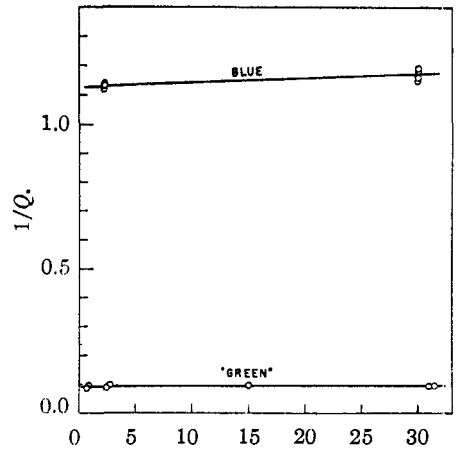


Fig. 7.—Quenching of blue and "green" acetone fluorescence as a function of absorbed intensity at constant pressure and temperature, high intensity: blue measured at 145° and 209 mm. pressure (not corrected for variable spectral sensitivity of photocell); "green" is total fluorescence at 25° and 164 mm., as measured; *ca.* 25% of observed deflection is due to blue.

tone molecules is accepted, the lifetime might be even longer.

The most significant aspect of the data concerning the green fluorescence is its decrease in intensity with increase in temperature even when biacetyl is known to be present. The decrease in intensity parallels semi-quantitatively the decrease in stability of the acetyl radical. This might indicate that the mechanism of excitation involves, in some way, the acetyl radical. The further fact that in starting with carefully purified acetone the blue decreases only 50% while the green increases from practically zero to a large value during continued exposure, indicates that the mechanism for the blue and the mechanism for the green are not identical and may possibly not be related.

The variation of $1/Q$ with pressure for the blue at 140° necessitates a marked sensitivity to collision at low pressures and the attainment of a statistical distribution among various energy levels, largely independent of pressure once the pressure reaches about 50 mm.

The principal data concerning the blue fluorescence may be described adequately by a series of simple steps resembling those used previously to describe other fluorescences[29,28] in which molecules are transferred from one state to another by collisions. This mechanism may be written

$$A + h\nu = A';\ k_1'I_a \quad (1)$$

$$A' = CH_3COCH_3 + h\nu;\ k_2(A') = I_b' \quad (2)$$

$$A' + A = 2A(\text{or } A + \text{dissociation products});\ k_3(A')(A) \quad (3)$$

$$A' + A = A'' + A;\ k_4(A')(A) \quad (4)$$

$$A'' = CH_3COCH_3 + h\nu;\ k_5(A'') = I_b'' \quad (5)$$

(29) J. P. Howe and W. A. Noyes, Jr., THIS JOURNAL, **57**, 1262 (1935).

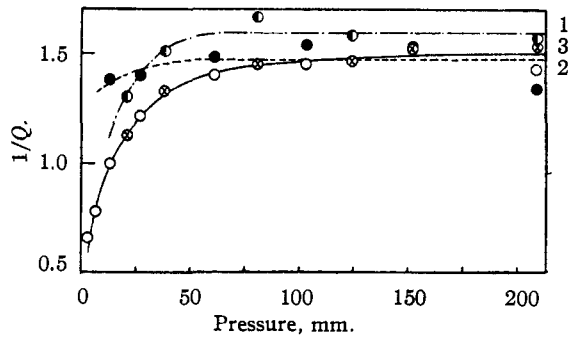


Fig. 8.—Quenching of blue fluorescence as a function of acetone pressure at 140°, wave length 3130 Å.: ◐, constant absorbed intensity (I_a = 2.5 ± 0.5 × 10^{11} $h\nu$/sec./cc.), values of I_a measured experimentally; ⊗, constant absorbed intensity; I_a calculated, assuming Beer's law; ●, constant incident intensity (I_0 = 4.9 × 10^{13} $h\nu$/sec./sq. cm.); I_a measured experimentally; O, constant incident intensity; I_a calculated. Curve 3 (solid) is drawn through both sets of points for which calculated values of I_a were used. The broken curves are for points using I_a measured experimentally, at constant I_a (curve 1) and constant I_0 (curve 2).

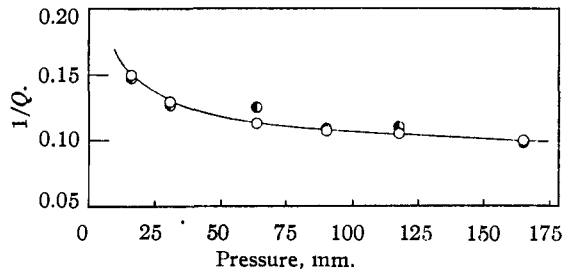


Fig. 9.—Quenching of total fluorescence (predominantly green) as a function of acetone pressure at 25° and constant absorbed intensity; I_a = 4 ± 1 $h\nu$/sec./cc.; wave length 3130 Å.

The constant k_1' indicates that only part of the molecules which undergo the act of absorption form excited molecules, or at least form excited molecules capable of the following reactions. From considerations of the photochemistry of acetone the vast majority must undergo a dissociation into CH_3CO and CH_3. From this series of equations one obtains the relationships

$$\frac{I_b' + I_b''}{I_a} = Q_b = \frac{k_1(k_2 + k_4(A))}{k_2 + k_3(A)} = \frac{k_1(1 + k_4(A)/k_2)}{1 + k_3(A)/k_2 + k_4(A)/k_2} \quad (6)$$

where $I_b' + I_b''$ = total quanta of blue radiation emitted per cubic centimeter per second and I_a is the number of quanta of incident radiation absorbed per cubic centimeter per second. If more states are used, equation (6) takes the form of a ratio of polynomials. When the pressure is very high, Q_b should be independent of pressure thus agreeing with the data in Fig. 8. If the pressure is extremely low Q_b should again be independent of pressure, but this levelling off will be important

only below 0.1 mm., a pressure lower than could be studied. With $k_3/k_2 = 0.24$, $k_4/k_2 = 0.088$, $k_4/k_3 = 0.37$, and $k_1 = 2.36$ (pressures in millimeters are used), equation (6) reproduces the experimental data well within experimental error. Since k_1 includes several factors it has no simple theoretical meaning, but the ratio of k_4 to k_3 means that the initially formed state is converted into the metastable state at about one third the rate it is deactivated. The metastable state must be very insensitive to collisions to explain the flat portion of the curve at high pressures, and hence no deactivation step is included for A″.

The absolute values of these constants cannot be calculated without making some assumptions. If every collision is assumed to cause the initially formed state to undergo either (3) or (4) and if the collision diameter is assumed to be 4×10^{-8} cm., $(k_3 + k_4)$ has the value 8×10^6 if the pressure in millimeters is used. Thus k_2 would be about 3×10^7 sec.$^{-1}$ and the mean life of the initially formed state would be about 3×10^{-8} sec. There is no way of estimating the mean life of the metastable state A″ due to the very small deactivating effect of collisions at high pressures.

The data on the quenching of the blue fluorescence by oxygen are not very extensive and, for various reasons, could not be made very precise. However, when the acetone pressure was 200 mm., 0.4 mm. of oxygen reduced the intensity by a factor of approximately 10. The following equations may now be added

$$A'' + O_2 = A + O_2;\ k_6(A'')(O_2) \qquad (7)$$

$$A' + O_2 = A + O_2;\ k_7(A')(O_2) \qquad (8)$$

and equation (6) becomes

$$Q_b = \left[\frac{k_1}{1 + (k_3/k_2 + k_4/k_2)(A) + k_7(O_2)/k_2}\right]\left[1 + \frac{k_4(A)/k_2}{1 + k_6(O_2)/k_5}\right] \qquad (9)$$

The term in k_7 should be negligible at the low pressure of oxygen used and hence from the data one can estimate k_6/k_5 to be 49 if the concentration of oxygen is replaced by millimeters pressure. If a collision diameter of 3×10^{-8} cm. is taken for collisions between metastable acetone molecules and oxygen, one can estimate k_6 and hence k_5. The latter is 10^5 sec.$^{-1}$ giving a mean life of the metastable acetone molecules of 10^{-5} second. This may be taken as a lower limit, and the actual value may be much larger if this state shows a low efficiency for quenching by oxygen molecules.

These lives of 10^{-8} and 10^{-5} second for the active and for the metastable molecules, respectively, are only orders of magnitude, but they do indicate that the picture of the blue fluorescence embodied in equations (1) to (5) is adequate to explain all of the known facts at constant temperature. The value of $1/Q$ is independent of intensity and independent of pressure at high pressures.

The mechanism embodied in equations (1) through (8) indicates that the ratio $(A'')/A$ is given by $k_4(A)/k_5 = 22\ P_{mm.}$ (in the absence of O_2). k_4 is probably more temperature dependent than k_5, and hence the fraction of A″ would increase with temperature. Since A″ is not appreciably deactivated by collisions, this would cause an increase in blue with temperature. This is contrary to the facts and hence the temperature effect must be explained in some other way. Equation (3) is the most logical step to use, particularly in view of the increase in quantum yields of decomposition with temperature. An activation energy of 2500 to 3000 cal. for reaction (3) would be adequate to explain the decrease in blue fluorescence with increase in temperature.

Finally it is necessary to include some deactivation of A″ by biacetyl since the blue does decrease slightly as the green increases in intensity. Due to its short life A′ would not be deactivated at low biacetyl pressures. If A″ is the only form deactivated in this way, the decrease in the blue is semiquantitatively explained.

Later work has shown structure to exist in the blue fluoresence. Thus dissociation accompanying the fluorescent act need not be postulated.

These general conclusions are the only ones warranted concerning the character of the blue fluorescence. Two types of information would still be desirable: (1) a study of the quenching down to very low pressures, *i. e.*, below 0.1 mm.; (2) a spectrographic study of the fluorescence at all pressures with high dispersion and high resolution. Both types of data would be exceedingly difficult to obtain due to the weakness of the blue fluorescence.

The interpretation of the green fluorescence must also be given in general terms. Two facts seem to be of paramount importance in this connection: (1) the intensity of the green is not dependent to any marked extent on the quantity of biacetyl once the latter has reached a value in the neighborhood of 0.1 mm.; (2) the intensity of the green decreases with increase in temperature even when biacetyl is known to be present and parallels at least qualitatively the decrease in stability of the acetyl radical.

Two general methods of exciting biacetyl to fluorescence when acetone is the absorbing molecule may be imagined; (1) inelastic collision of the second kind; (2) a recombination of two free radicals using biacetyl as the third body.

The very gradual decrease in intensity of the blue and the rapid decrease in the green with rise in temperature indicate that the two processes are not completely dependent on each other. The effect of pressure on $1/Q$ (Fig. 9) is also not at all similar to the effect on the blue fluorescence and indicates that collisions tend to enhance the fluorescence. This resembles the behavior of the fluorescence of pure biacetyl when excited by radiation of wave length 3660 Å.[15,19] and is best explained by assuming that the level initially formed is capable of predissociation and that fluorescence only occurs after loss of some energy through collisions.

If the absence of green fluorescence at 140° is due directly or indirectly to the instability of the acetyl radical, the three body process

$$CH_3 + CH_3CO + B = B' + CH_3COCH_3; \quad k_8(CH_3)(CH_3CO)(B) \quad (10)$$

must be responsible, where B is a molecule of biacetyl. The effect of oxygen in quenching the green would be due, in that event, to reaction with free radicals.

A complete set of equations satisfying the photochemical as well as the fluorescence data can be written down using equation (10) as the means of producing excited biacetyl. The resulting equation for $1/Q$ is, however, very complex and while it has the correct form there is no means of showing that it is a unique solution to the problem. Since $1/Q$ decreases slightly with increase in pressure, it is necessary to postulate that the active molecule B′ can dissociate unless it is stabilized by collisions. At higher pressures $1/Q$ is practically independent of pressure so that an additional state B″ (or perhaps several additional states) must be postulated. Some of these would be metastable and incapable of fluorescence. The fluorescing states would be converted into the other and vice versa by collisions. These suggestions agree with those made by Almy and coworkers.[15]

If a mechanism for exciting biacetyl based on collisions of the second kind is used, the decrease in green intensity with increase in temperature would be ascribed to two effects: (1) a decrease in the concentration of activated and metastable acetone molecules (A′ and A″, respectively); (2) an increased tendency for the activated or metastable biacetyl molecules to decompose. The first of these effects is insufficient in itself to provide an adequate explanation since the decrease in intensity of the blue fluorescence is explained by some inhibiting step with an activation energy of 2500–3000 cal., while the green demands a step with an activation energy of 4500–5000 cal.

Since it has been shown that biacetyl fluorescence is normally quenched when excited by 4060 and 4370 Å. radiation,[15] whereas collisions enhance the fluorescence when it is excited by 3660 Å. radiation,[15,19] one can estimate a maximum activation energy required to raise the fluorescing molecules to such a state that they can predissociate. Taking the difference in calories per gram molecule corresponding to 4060 and 3660 Å. quanta, respectively, one finds 7600 calories. The correct figure may be less. Another guess can be made from the absorption spectrum of biacetyl described by Henri[30] who gives the longest wave absorption band as 4670 Å. and the onset of predissociation as 4400 Å. The difference corresponds to 3900 cal. per molecule, and this, if the spectrum has been correctly interpreted, should correspond to the minimum activation energy required to bring an excited non-vibrating molecule to the predissociating state. These figures, while probably inaccurate, lend some small support to the interpretation of the temperature effect on the fluorescence.

Several authors have studied the photochemistry of biacetyl.[31,32,33] A detailed interpretation of the data is not possible because many processes must be involved. The low yield at room temperature may be due to a recombination reaction and part of the increase with temperature due to the instability of the acetyl radical. However, at long wave lengths (>3660 Å.) where fluorescence occurs, the effect of temperature on activated molecules must be considered.

The effect of oxygen on green fluorescence is to be ascribed to two effects: (1) inhibition of biacetyl synthesis through reaction with acetyl radicals; (2) inhibition of the fluorescence even when biacetyl is present. The latter effect, in turn, must be due to two causes: (1) decrease in the number of excited or metastable acetone molecules if the energy transfer is by collisions of the second kind or reaction with radicals if excitation is by some process, such as equation (10); (2) quenching of excited or metastable biacetyl molecules. There is ample evidence for both of these steps in the effect of oxygen on the blue and on the fluorescence of pure biacetyl.[15] Undoubtedly both effects are important.

It should be emphasized finally that while these fluorescence studies throw much light on the photochemistry of acetone, particularly with long exposures, they do not affect in any essential way the mechanism previously presented for the photochemistry of acetone.[9] No precise estimate of absolute fluorescence efficiency can be given, but that of the blue does not exceed one or two per cent. and may be much less.

Summary

1. The quenching of the "blue" and "green" fluorescences of acetone has been studied as a function of intensity, pressure, added oxygen, and temperature.

2. Since screens were used to vary intensity, the variation with intensity is valid only if the excited molecules or radicals involved have long lives. This is probably true for the "green" but may not be true for the "blue." No variations of quenching with intensity were observed.

3. The fluorescent efficiency of the "blue" decreases as the pressure increases and approaches a constant value. That of the green increases as the pressure increases and also approaches a constant value.

4. The efficiency of the "blue" decreases gradually with increase in temperature and is still

(30) V. Henri, "La Structure des Molecules," Gauthier-Villars et Cie., Paris, 1925.

(31) J. G. Roof and F. E. Blacet, THIS JOURNAL, **63**, 1126 (1941).

(32) R. G. W. Norrish and F. W. Kirkbride, *Trans. Faraday Soc.*, **27**, 404 (1931).

(33) H. W. Anderson and G. K. Rollefson, THIS JOURNAL, **63**, 816 (1941).

20% of its room temperature value at 200°. The green decreases much more rapidly and is practically absent at 135°.

5. Alternative explanations of the various phenomena are discussed, and several suggestions concerning mechanism are made. There must be two states of acetone, one with a much shorter life than the other. The biacetyl may be excited by either of two processes: (a) collision of the second kind; (b) radical recombination using biacetyl as the third body. In either case the "active" biacetyl molecules must have a greater probability of decomposition at high temperatures than at low.

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULUTRE, UNIVERSITY OF CALIFORNIA]

Interaction of Ions and Dipolar Ions. IV. The Solubility of Cupric Iodate in Glycine and in Alanine Solutions

BY R. M. KEEFER

In previous communications[1,2] it was shown that the solubility of certain 1–1 and 2–1 type salts in dipolar ion solutions could be expressed by equations of the type

$$\frac{1}{Z_1Z_2}\log\frac{S}{S_\infty} = 0.506\left(\frac{78.54}{D_s}\right)^{3/2}\frac{\sqrt{\mu}}{1+A\left(\frac{78.54}{D_s}\right)^{1/2}\sqrt{\mu}} + 0.0625\frac{R^2}{a_{id}}[HR^\pm] \quad (1)$$

where Z_1 and Z_2 are the valences of the ions; S_∞ is the theoretical solubility at $\mu = 0$ and $[HR^\pm] = 0$; D_s is the dielectric constant of the solution; A is $0.3288a_i$ where a_i is the distance of closest approach of the ions; R is the dipole distance in the dipolar ion; a_{id} is the distance of closest approach of an ion to a dipolar ion; and $[HR^\pm]$ is the concentration of the dipolar ion. The solubility of silver iodate and lead iodate in glycine and alanine solutions[3] is much higher than would be predicted by eq. (1). The increased solubility was accounted for by assuming complex ions consisting of one negative ion of the amino acid to one silver or lead ion. This investigation was undertaken to obtain information on the stability of a complex between one negative ion of the amino acid[4] and cupric ion.

Experimental

Cupric Iodate.—Equal volumes of 0.2 M potassium iodate and 0.1 M cupric nitrate were added dropwise with constant stirring to 3 liters of water at 60°. After six hours the precipitate was filtered off and allowed to equilibrate with water overnight. The precipitate was sedimented several times and the smaller particles were discarded. The preparation was air dried before using. After drying for two hours at 250–270° the dried cupric iodate when analyzed iodometrically was 100.1% cupric iodate.

The solubility determinations and general technique have been described in a previous communication.[1] The iodometric determinations were modified for the presence of cupric ion using the method of Foote and Vance.[5] Duplicate solubility determinations agreed to 2 parts in 1000.

The pH of the solutions was determined using a Model G Beckman pH meter and is accurate to ±0.01 pH unit. The definition of pH used in this work is the negative logarithm of the hydrogen ion activity.

Results

The solubility (moles/1000 g. H_2O) of cupric iodate in potassium chloride solutions at 25.00° is given in Table I. The solubility of cupric iodate in water is much lower than the value (3.693×10^{-3} M) reported by Peterson and Meyers.[6] Column 3 of Table I gives the solubility of cupric iodate calculated by means of equation (2).

$$\log [Cu^{++}][IO_3^-]^2 = -7.1353 + \frac{3.036\sqrt{\mu}}{1+1.08\sqrt{\mu}} \quad (2)$$

The distance of closest approach of the ions is then 1.08/0.3288 or 3.28 Å.

TABLE I

SOLUBILITY OF CUPRIC IODATE IN POTASSIUM CHLORIDE SOLUTIONS AT 25°

(M is Moles/1000 g. H_2O and S is M of Cupric Iodate)

KCl, M	$Cu(IO_3)_2$, $M \times 10^3$	Calcd. $Cu(IO_3)_2$, $M \times 10^3$
0	3.245	3.243
0.00501	3.398	3.396
.01002	3.517	3.521
.02005	3.730	3.730
.03511	3.975	3.969
.05017	4.166	4.166
.07529	4.453	4.454
.1005	4.694	4.697

Table II gives the solubility of cupric iodate in glycine and in alanine solutions together with the pH of the resulting solution. Since the pH values are all less than the isoelectric point of the amino acids (6.1), it is evident that reactions are taking place which produce hydrogen ion. Assuming

(1) Keefer, Reiber and Bisson, THIS JOURNAL, **62**, 2951 (1940).
(2) Keefer and Reiber, *ibid.*, **63**, 3504 (1941).
(3) Keefer and Reiber, *ibid.*, **63**, 689 (1941).
(4) Gould and Vosburgh, *ibid.*, **64**, 1630 (1942).
(5) Foote and Vance, *Ind. Eng. Chem., Anal. Ed.*, **8**, 119 (1936).
(6) Peterson and Meyers, *ibid.*, **52**, 4853 (1930).