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

The Relative Intensities of Fluorescence and Phosphorescence in Biacetyl Vapor[1]

BY HIDEO OKABE AND W. ALBERT NOYES, JR.

RECEIVED AUGUST 20, 1956

A technique is described for measuring the relative intensities of emission from biacetyl vapor in the blue (fluorescence) and in the green (phosphorescence) parts of the spectrum when exciting wave lengths are around 4358 and 3650 Å., respectively. In pure biacetyl at 26° and 42 mm. pressure the integrated ratio of green to blue is 58 (±8):1. This ratio is unaffected by change in wave length and by the addition of acetone, benzene or methyl chloride. The ratio decreases as the temperature is raised and decreases rapidly to zero upon addition of oxygen. The state from which phosphorescence occurs must be formed from the electronic-vibration state from which fluorescence occurs by a step which parallels and is independent of fluorescence. Both rates must apparently be collision independent under the conditions studied. Dissociation must occur from upper vibration levels of the singlet state although the data do not provide conclusions about details of this process. Biacetyl emission in biacetyl–acetone mixtures irradiated at 3130 Å. (absorbed mainly by the acetone) leads at room temperature to a preferential excitation of phosphorescence rather than fluorescence. The previously proposed mechanism can account for these facts.

The fluorescence and phosphorescence of biacetyl have been studied extensively for many years. Photochemical dissociation, fluorescence and phosphorescence may be correlated in terms of a mechanism which seems to be applicable to several simple ketones.[2] Fluorescence and phosphorescence for a great many organic molecules may be described in terms of an upper (singlet) electronic state formed from the ground (singlet) state by the absorption of radiation. Fluorescence results from emission of radiation when molecules in the lower vibration levels of this upper (singlet) state jump to various vibration levels of the ground state. There is also an upper (triplet) state from which phosphorescence occurs by jump to the ground state. This upper (triplet) state must be formed from the upper (singlet) state. In the case of the simple ketones (as well as for most other carbonyl compounds) complications arise from the fact that dissociation proceeds concurrently with fluorescence and phosphorescence.[3,4]

The ratio of phosphorescent to fluorescent intensity is of importance to an understanding of the problem of emission and of photochemical dissociation.[5] This seems to have been done first for biacetyl by Doolittle.[5a] This was done by photographic photometry and although integrated intensities were not compared, there is general agreement between Doolittle's work and the present work. She could find no evidence for direct absorption from the ground state to the upper triplet state.

Since the sum of the quantum yields of fluorescence, phosphorescence and dissociation is far less than unity when radiation centering around 4358 and 3650 Å. is used, a large fraction of the absorbed energy must be dissipated in other ways.

The main missing information concerns the level or levels from which dissociation occurs, the level or levels of the upper singlet state from which transfer to the triplet state occurs and the "order" of this transfer reaction, and the mechanism by which radiation absorbed by acetone excites the fluorescence and phosphorescence of biacetyl in a mixture of acetone and biacetyl. This work attempts to supply some of the missing information.

Experimental

The purification of biacetyl[6] and acetone[7] has already been described. Mallinckrodt A. R. benzene was dried over anhydrous calcium sulfate and fractionated in a Todd column having 30 plates with reflux ratio of 10:1. It was further purified by bulb-to-bulb distillation in a stopcock-free vacuum line, degassed and stored behind a mercury cutoff. Tank methyl chloride supplied by the Matheson Company, stated to be 99.5% pure, was further purified by distillation from a bulb kept at Dry Ice temperature to a bulb kept at liquid nitrogen temperature. After repeated degassing the middle third was retained.

The incident beam from a General Electric AH-6 arc passed through a diaphragm, was collimated by a quartz lens of 120 mm. focal length, passed through various combinations of filters, and was focused by another quartz lens of 110 mm. focal length into a narrow beam about 1 mm. in diameter at the center of the cell. The emitted radiation passed through a glass lens of 50 mm. focal length and was introduced to the slit of a Bausch and Lomb constant deviation glass spectrograph, which has a reciprocal dispersion of 42 Å./mm. at 5000 Å. The glass lens was placed in such a position as to bring the image of the beam to the collimator lens of the spectrograph in order to get a uniform illumination of the slit.[8]

Filter combinations used in the present work were: for 4358 Å., 24 mm. path length of saturated sodium nitrite solution and 15 mm. path length of copper ammonium sulfate complex solution. The latter solution was made by mixing 34.4 g. of $CuSO_4 \cdot H_2O$, 50 cc. of concentrated NH_4OH (28% NH_3) and 425 cc. of water; for 3650 Å., 3 mm. thickness of Corning glass No. 5840. Since the emission is too weak to use monochromatic light for 3130 Å., a combination of 3 mm. Corning Glass No. 9863 and 15 mm. of 1.78 *M* $NiCl_2$, which transmits some 3341 Å. and some radiation of shorter wave length than 3130 Å., was employed. It was found for the above combination that the spectral distribution of the emission was the same as when the Hunt and

---

[1] This work was supported in part by contracts with the Office of Naval Research, United States Navy, and the Chemistry Division, Air Force Office of Scientific Research, United States Air Force. The material in this article may be reproduced or used in any way by the United States Government.

[2] A review of this subject has recently been presented: W. A. Noyes, Jr., G. B. Porter and J. E. Jolley, *Chem. Revs.*, **56**, 49 (1956). References to earlier literature are given in this review and only those relating specifically to the present work will be given at this time.

[3] Space will not permit a detailed bibliography of fluorescence and phosphorescence of polyatomic molecules to be given. W. West has recently published a good review of the subject: W. West, "Fluorescence and Phosphorescence," Chapter VI of "Chemical Applications of Spectroscopy," edited by A. Weissberger, Interscience Publishers, New York, N. Y., 1956, p. 707.

[4] Two papers which discuss the general problem of the relationship of upper singlet and triplet states are: M. Kasha, *Chem. Revs.*, **41**, 401 (1947); *Disc. Faraday Soc.*, **9**, 14 (1950).

[5] *Cf.* D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

[5a] Jane E. Doolittle, M.S. Thesis, University of Rochester, 1949. This work was performed under the direction of Professor A. B. F. Duncan.

[6] H. J. Groh, Jr., *J. Chem. Phys.*, **21**, 674 (1953).

[7] G. W. Luckey and W. A. Noyes, Jr., *ibid.*, **19**, 227 (1951).

[8] G. R. Harrison, R. C. Lord and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 128.

Davis filter,[9] which transmits principally 3130 Å., was used.

The blue to green emission ratio was compared arbitrarily as the intensity ratio at 4700 and at 5120 Å. on the spectrum. Because of the proximity of the exciting light (4358 Å.) to the blue fluorescence, it was necessary to minimize the scattering of the exciting light. Therefore the outside of the cell wall was painted black, the windows kept clean, and the emission measured at a right angle to the incident beam. Eastman Kodak 103_a-B plates were used.

In order to avoid the reciprocity law failure, a step wedge,[10] which reduces the strong green phosphorescence to almost the same intensity as the weak blue fluorescence, was used at the spectrograph slit. The wedge has five steps of 1 mm. width each. The density of each step was measured by a Sinclair Smith microdensitometer under the parallel incident beam through Kodak Wratten gelatin filter No. 61 in order to get the same transmission value as for the green phosphorescence. The density of the wedge thus obtained ranged from 1.22 to 2.19. The successive density increment of the step was about 0.25. The various intensity levels of the emission for each step were thus obtained along the slit length and the corresponding spectrograms of various densities taken. The densities at 5120 Å. on a spectrogram (the first intensity maximum) corresponding to each step were plotted against the densities of the steps. The densities at 5570 Å. (the second intensity maximum) were also plotted on the same curve to supplement the lower density region. The wave lengths of the spectrogram were determined by a Hartman Dispersion formula using scattered exciting light as a standard. The density equal to that at 4700 Å. was found on the curve and the corresponding density of the step was obtained. The value gives the logarithm of the green to blue arbitrary ratio. Since the intensity ratio was the main interest in this work, a relatively large slit width of 0.55 mm. was used. The exposure time was chosen to get the density of 0.6, approximately, for the blue fluorescence. It ranged from half an hour to as much as 7 hours.

To obtain the integrated intensity ratio of the green to blue emission at room temperature, three 2 minute and one 40 and one 50 minute exposures were made at a pressure of 42 mm. to obtain the green and the blue emission spectra, respectively, with 4358 Å. excitation, since the densities of the blue and green regions are too different to compare under the same exposure time. The characteristic curve of the plate was obtained by the intensity variation method.[11] The correction for the reciprocity law failure for the blue fluorescence was made by multiplying by 1.4.[12] After the correction of the intensities for the blue and green emissions obtained from the characteristic curve into the same exposure time, they were plotted against the wave lengths and the areas under the curve were compared. Self-absorption of the emission by the vapor was insignificant and no correction was made.

The vacuum line and the gas techniques follow the customary procedures and will not be described here.

Results

(a) **Effect of Temperature.**—In general, previous observations on the effect of temperature[2] have been confirmed. Fluorescence of biacetyl vapor is excited by wave lengths from 4357 to 3650 Å. but is not excited by 3130 Å. Both the blue (fluorescence) and green (phosphorescence) regions are independent of exciting wave length. Fluorescence starts near 4400 Å., reaches a maximum at about 4600 Å. and changes little from there to 4800 Å. At longer wave lengths there are three maxima at 5120, 5600 and 6000 Å., respectively, with relative intensities of 22, 6 and 1.

The positions of the maxima and their relative intensities do not change with temperature but the green portion (phosphorescence) decreases in intensity with rise in temperature much more rapidly than does the blue (fluorescence).

The integrated intensity ratio of green to blue emission at 26 ± 2° and 42 mm. was 58 ± 8 to 1. Under the same conditions the arbitrary ratio compared at 5120 and 4700 Å. for the green and blue, respectively, was 103 to 1. Hence the arbitrary ratios measured at the above wave lengths can be converted to the integrated ratio by multiplying by a factor of 0.56, because the character of the emission spectrum is independent of pressure and of temperature.

The following integrated ratios of intensities of green to blue when excited by 4358 Å. have been observed in biacetyl vapor: 60:1 (26 mm., 26°); 30:1 (25 mm., 84°); 7:1 (25 mm., 117°); 4.3:1 (26 mm., 152°); 1.7:1 (28 mm., 182°). If the intensity of the green at 26° is arbitrarily placed at 60, Coward's results[13] showed the relative intensity of the green to be 60, 30, 13 and 4.8 at the first four temperatures. Thus the intensity of the blue probably changes little with temperature.

(b) **Effects of Wave Length and Pressure at 26 ± 2°.**—Because of the low absorption by biacetyl vapor at 3650 Å. exposures up to several hours were necessary to obtain sufficient blackening of the photographic plates to measure. The following integrated ratios of intensities were obtained at 26 ± 2° with 3650 Å. excitation: 57:1 (13 mm.); 51:1 (13 mm.); 60:1 (34 mm.); 59:1 (34 mm.); 61:1 (45 mm.).

The following ratios were obtained at 4358 Å. at 26 ± 2° at a series of pressures: 62:1 (5 mm.); 62:1 (5 mm.); 56:1 (5 mm.); 65:1 (10 mm.); 59:1 (11 mm.); 60:1 (25 mm.); 53:1 (31 mm.); 56:1 (35 mm.); 55:1 (39 mm.); 56:1 (43 mm.); 59:1 (44 mm.). Exposure time was varied from 30 minutes to 9 hours.

The grand average of the integrated ratio of green to blue fluorescence at 26 ± 2° is 58.4 ± 2.5:1, independent of pressure, time of exposure and incident wave length.

(c) **Effect of Added Gases.**—Since the biacetyl fluorescence is excited in an acetone–biacetyl mixture by 3130 Å. radiation which is absorbed almost solely by the acetone, it is possible that acetone would be an efficient quencher for biacetyl fluorescence. Benzene was studied because it is a symmetrical molecule which does not absorb at either wave length used. A molecule with a relatively heavy atom might affect the green to blue ratio which varies with the degree of spin–orbit interaction. Methyl chloride was used for this purpose.

Table I shows the intensity ratio in biacetyl foreign gas mixtures. The gases studied in the present work do not affect the ratio.

(d) **Biacetyl Emission Sensitized by Acetone.**—A mixture of biacetyl and acetone exposed to 3130 Å. radiation shows the characteristic emission of biacetyl whereas pure biacetyl does not emit when exposed to that wave length. This phenomenon

---

(9) R. E. Hunt and W. Davis, Jr., This Journal, **69**, 1415 (1947).

(10) The authors wish to thank Dr. G. W. Luckey for the supply of this wedge.

(11) The authors wish to thank the Institute of Optics of the University of Rochester and Mr. J. N. Pike for the loan of the apparatus to measure the characteristics of the plate.

(12) "Kodak Photographic Plates for Scientific and Technical Use," Eastman Kodak Company, Rochester 4, N. Y., 1953, pp. 7–8.

(13) N. A. Coward and W. A. Noyes, Jr., *J. Chem. Phys.*, **22**, 1207 (1954).

TABLE I

EFFECT OF FOREIGN GAS ON RATIO OF GREEN TO BLUE EMISSION FROM BIACETYL

$T = 26 \pm 2°$. A.I.R. is the arbitrary intensity ratio. I.I.R. is the integrated intensity ratio.

Biacetyl pressure, mm.	Foreign gas pressure, mm.	Wave length, Å.	A.I.R. green to blue	I.I.R. green to blue
		A. Acetone		
9	128	4358	90:1	55:1
10	124		95:1	58:1
31	0		95:1	58:1
26	90	3650	104:1	57:1
34	0		105:1	58:1
		B. Benzene		
11	66	4358	110:1	64:1
10	75		100:1	58:1
11	70		105:1	61:1
43	0		100:1	58:1
		C. Methyl chloride		
21	266	4358	97:1	59:1
15	295		105:1	61:1
13	568		94:1	57:1
31	0		95:1	58:1
		Grand av.		(58.0 ± 1.4):1

has been known for some time[2,14] but its detailed explanation has not been possible. A study of the intensity distribution with this kind of excitation might be of considerable help in this connection.

Both biacetyl and acetone show emission in the blue. The acetone blue fluorescence extends from about 3800 to about 4800 Å. with a broad maximum between 4500 and 4600 Å.[15] Pure biacetyl emission begins about 4400 Å. and extends to longer wave lengths. The blue emission must therefore be considered to be a mixture of the two. The green to blue intensity ratios were measured at 5120 and 4700 Å. Since there is an unknown amount of acetone blue fluorescence mixed with the biacetyl blue, the actual arbitrary intensity ratios should be greater if a proper correction could be made for the acetone emission. If the ratio I_{4700}/I_{4350} (where I_{4700} is the intensity at 4700 Å. and I_{4350} is the intensity at 4350 Å.) is assumed to be the same for acetone in the mixture as it is for pure acetone, then one can calculate the correction which must be made at 4700 Å. for the acetone emission. This is so because there is no biacetyl emission at 4350 Å. Actually this correction may be too large because biacetyl may reduce acetone emission at 4700.

The arbitrary intensity ratio of green to blue uncorrected for acetone emission at 4700 Å. will be a minimum value and the one corrected for acetone emission will be a maximum. It should be noted[16] that biacetyl suppresses the phosphorescence of acetone.

At 26° the arbitrary intensity ratio with 4358 Å. excitation in pure biacetyl was 95:1. The results in acetone–biacetyl mixtures are as follows: wave length, 3130 (absorbed almost entirely by the acetone); $T = 26 \pm 2°$; biacetyl pressure, 22 mm., acetone pressure, 106 mm., A.I.R. (uncorrected), 180:1; A.I.R. (corrected for blue emission by acetone): 250:1; biacetyl pressure, 32 mm., acetone pressure, 53 mm., A.I.R. (uncorrected), 160:1; A.I.R. (corrected), 180:1.

These figures indicate that at 26° the ratio of green to blue is two or more times as great when emission is sensitized by acetone as it is when radiation is absorbed directly by the biacetyl.

An attempt was made to study the acetone sensitized fluorescence of biacetyl at higher temperatures where phosphorescence from both biacetyl and from acetone has become extremely weak. At 150° acetone showed only the very faint blue fluorescence extending from 4100 to 4800 Å. with a broad maximum about 4400 Å. This emission undoubtedly arises from the short lived state of acetone (fluorescence).[2] When 15 mm. of biacetyl was added to 200 mm. of acetone at 150°, the acetone fluorescence was absent but the biacetyl blue fluorescence appeared, beginning about 4400 Å., reaching a more or less constant intensity from about 4550 to about 4900 Å. Pure biacetyl even at 52 mm. pressure showed no trace of fluorescence when irradiated at 3130 Å. Thus the disappearance of the acetone fluorescence and the appearance of biacetyl emission afford strong contributory evidence that the fluorescing state or states of acetone participate in the excitation of the biacetyl. The possibility is not completely excluded that some additional excited states may be responsible for the excitation of the biacetyl molecules.

Discussion

There has evolved during the past twenty years an energy level scheme which seems to account satisfactorily for the fluorescence and phosphorescence of many polyatomic molecules.[2–4] This scheme when coupled with the recent elucidation of the absorption spectrum of biacetyl[17] affords a basis for discussion of the results herein reported. The case of biacetyl is differentiated from that of many other polyatomic molecules by the fact that photochemical dissociation occurs along with fluorescence and phosphorescence. The two types of phenomena have been related in a broad way[18] but certain details relative to internal conversion and dissociation remained to be supplied.

For the sake of convenience of discussion we will employ the energy level diagram in Fig. 1.[19] The ground electronic state is designated as X and its various vibration levels are designated X_0, X_1, ... ,X_n. Y is the electronic state formed by absorption of radiation and its vibration levels are designated Y_0, Y_1, ... ,Y_n. Y is probably a singlet state with a short life. Z is the state from which phosphorescence occurs and its vibration levels are Z_0, Z_1 , . . . ,Z_n. It is almost certainly a triplet state.[4,17] (Absorption and emission spectra of biacetyl are shown in Fig. 2.)

---

[14] M. S. Matheson and J. W. Zabor, *J. Chem. Phys.*, **7**, 436 (1939).

[15] G. W. Luckey, A. B. F. Duncan and W. A. Noyes, Jr., *ibid.*, **16**, 407 (1948).

[16] G. W. Luckey, Ph.D. thesis, *University of Rochester*, 1950.

[17] J. W. Sidman and D. S. McClure, THIS JOURNAL, **77**, 6461, 6471 (1955).

[18] G. F. Sheats and W. A. Noyes, Jr., *ibid.*, **77**, 1421, 4532 (1955).

[19] To avoid confusion the various levels are given the same symbols as in ref. 2.

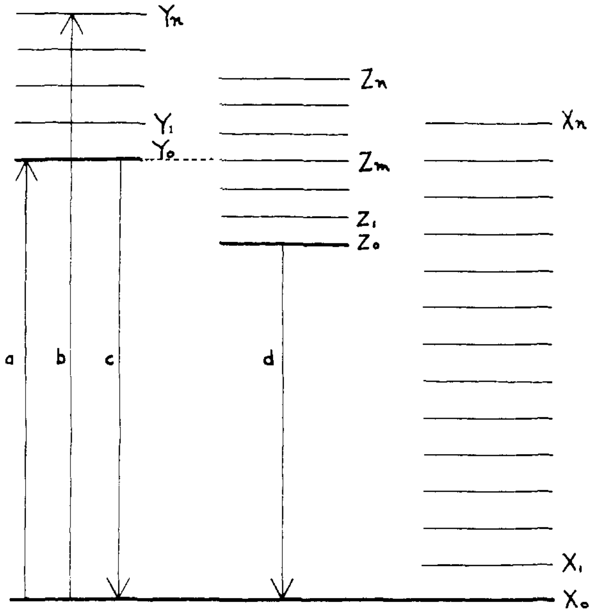

Fig. 1.—Energy level diagram: a, absorption at 4358 Å.; b, absorption at 3650 Å.; c, fluorescent emission; d, phosphorescent emission.

The two cases of absorption at 4358 Å. and of absorption at 3650 Å. differ in the sense that at the longer wave length there is very little self quenching and the fluorescence efficiency is nearly independent of pressure, whereas at the shorter wave length increase in pressure is accompanied by increase in fluorescence efficiency and decrease in photochemical primary quantum yield.[2] The (0, 0) band for the X → Y transition has been placed by Sidman and McClure[17] at about 4370 Å. in the crystal at 20°K. Excitation by 4358 Å. must, therefore, raise molecules in levels near X_0 to states near Y_0. At 3650 Å. much higher Y levels must be produced. Nevertheless neither the intensity distribution in the green nor the integrated ratio of green phosphorescent intensity to blue fluorescent intensity changes with wave length. Moreover the intensity distribution in the green does not change with temperature.

The above facts support strongly the following conclusions: (a) the fluorescence (blue) occurs by transitions from levels near Y_0 to various X levels and the phosphorescence (green) occurs by transitions from levels near Z_0 to various X levels; (b) vibration energy must be lost by collision to cause transitions from Y_n to levels near Y_0 so rapidly that essentially no radiative transitions from Y to X levels occur except from levels near Y_0; (c) the transition from Y_0 to a Z level must be followed by loss of vibration energy so rapidly that this step is in fact not reversible; (d) the nature of the internal conversion step cannot be specified from these data.

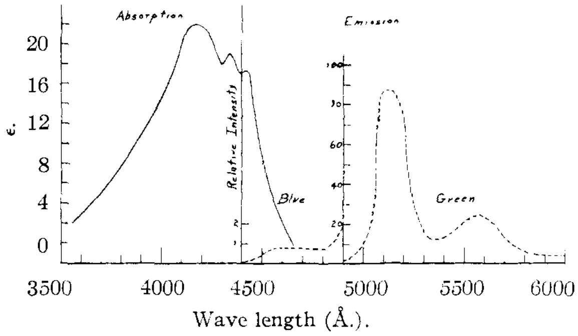

Fig. 2.—Absorption and emission spectra of biacetyl. The solid curve at the left shows the variation of extinction coefficient (defined by the equation $\epsilon\ d\ C = \log_{10}\ (I_0/I_{tr})$ where d is thickness in centimeters, C is concentration in moles per liter, I_0 is incident intensity and I_{tr} is transmitted intensity) with wave length. The data are recalculated from G. N. Lewis and M. Kasha, THIS JOURNAL, **67**, 994 (1945). The emission (dotted lines) is shown in two parts because the blue is very weak compared to the green. Hence the blue is shown with a vertical scale ten times that for the green. The emission data have been observed many times and the scale is purely a relative one. Temperature in both instances 26°. Solid line, molal extinction curve of biacetyl vapor at 27° redrawn from the work of Lewis and Kasha; dotted line, relative intensity curve of biacetyl blue fluorescence and green phosphorescence at 26°.

The primary photochemical quantum yield at 4358 Å. is virtually zero at zero intensity at 25°[18] but it increases with increase in temperature. At 3650 Å. the primary yield is low, increases at low pressures, increases with rise in temperature. At both wave lengths and at all temperatures studied the sum of the fluorescence yield and the photochemical primary yield is far less than unity. Thus a large fraction of the absorbed energy must be dissipated by some process other than dissociation and light emission. Since there is little self quenching at 4358 Å. of either the fluorescence or the phosphorescence, this dissipation of energy cannot occur from either Y_0 or Z_0 by a process whose rate is controlled by collisions. Since oxygen destroys the green emission with virtually no effect on the intensity of the blue one may draw the following conclusion: Internal conversion from Y_0, fluorescence from Y_0 and formation of Z levels from Y_0 occur as parallel reactions whose relative rates are independent of pressure of biacetyl and of added gases (oxygen, methyl chloride, benzene, acetone). However this does not prove that there is internal conversion from Y_0 and in fact internal conversion may occur from either Y_0 or Z_0 or both. The data at 3650 Å. also demand that there be internal conversion from higher Y levels.

The facts exclude the conversion of Y_n to Z_n followed by loss of vibration energy through collision to form Z_0 since this process would have to be parallel to vibration loss through collision to convert Y_n to Y_0.

The steps in the mechanism pertinent to the present discussion will be given and discussed

$$X_0 + h\nu = Y_n \tag{1}$$
$$Y_n = D \tag{2}$$
$$Y_n = X \tag{3}$$
$$Y_n + M = Y_0 + M \tag{4}$$
$$Y_0 = Z_m \tag{5}$$
$$Z_m + M = Z_0 + M \tag{6}$$
$$Y_0 = X + h\nu^* \tag{7}$$
$$Z_0 = X + h\nu^{**} \tag{8}$$

where n and m as subscripts denote vibration energy levels other than the lowest of the corresponding electronic state, M denotes any colliding molecule (either of biacetyl or of an added gas), D denotes products of the primary photochemical dissociation. The level Z_m has the same total energy as Y_0. The reverse of 5 seems to be unimportant because of the speed of 6. Step 3 is necessary since the intercept of $1/\phi$ *vs.* (B) at 3650 Å. is far greater than unity. (ϕ is the primary photochemical quantum yield.) The data do not provide positive information as to whether 3 is written correctly as a single step or whether it should be broken down into a series of transitions (*e.g.*, Y to Z followed by Z to X); ((B) = biacetyl concentration).

Steps which are logically excluded by the data include $Y_n = Z_n$ followed by $Z_n + M = Z_0 + M$. Moreover $Y_0 = Z_m$ must be first order and not depend on (B). It should be noted that the molecule M may not be a molecule such as oxygen or iodine which might react with or exert a specific deactivating effect on the Z levels. Such reactive molecules constitute special cases which must be treated separately. Steps 7 and 8 denote fluorescence and phosphorescence, respectively.

The relationship of spin–orbital coupling to the mechanism of fluorescence quenching has been discussed by Kasha.[20] He shows that perturbation of spin–orbital coupling may occur in the liquid phase which will in some instance enhance considerably the singlet–triplet absorption. By inference collisional effects might lead to perturbations which would markedly affect the ratio of phosphorescence to fluorescence, but these effects would doubtless be difficult to observe in the gas phase at the pressures used in the present experiments. Methyl chloride did not affect the ratio and molecules with heavier atoms than chlorine were not tried because their physical properties made their use difficult or impossible. Thus the negative results with methyl chloride have only minor importance.

It has been known for many years[2] that the paramagnetic gases nitric oxide and oxygen exert specific quenching effects on the phosphorescence. Preliminary data tend to indicate that the effect with biacetyl is mainly due to a real chemical reaction but this subject needs further investigation.

Deactivation steps such as $Y_0 + M = X + M$ and $Z_0 + M = X + M$ seem to be unimportant if M is acetone, biacetyl, benzene or methyl chloride since these molecules affect little or not at all the intensity of the emission. It should be noted also that we have not included the second-order step which involves apparently two molecules in the Z_0 state. This process is responsible for photochemical dissociation at room temperature at 4358 Å.[18] and for the effect of intensity on the phosphorescent yields as observed first by Kaskan and Duncan.[21]

The primary photochemical yield increases with increase in temperature and yet there seems to be relatively little change in the fluorescence efficiency. This apparently makes it necessary to add the reaction

$$Z_0 = D \qquad (9)$$

Quite possibly collisions will determine the rate of 9 at least at low pressures but collisions may be expected both to activate Z_0 and to deactivate higher vibration levels of Z so that the over-all rate constant should attain a constant value at moderate pressures in the same sense as do unimolecular reactions. Equation 9 must have an appreciable activation energy to agree with the facts.[2]

The three efficiency equations may now be written

$$I_p/I_a = \frac{k_8(Z_0)}{I_a} = \frac{k_5}{k_5 + k_7 + k_{13}} \times \frac{\Sigma k_4^i\ (M)}{k_2 + k_3 + \Sigma k_4^i\,(M)} \times \frac{k_8}{k_8 + k_{14}} \qquad (10)$$

$$I_f/I_a = \frac{k_7(Y_0)}{I_a} = \frac{k_7}{k_5 + k_7 + k_{13}} \times \frac{\Sigma k_4^i\ (M)}{k_2 + k_3 + \Sigma k_4^i\,(M)} \qquad (11)$$

$$\phi = \frac{k_2}{k_2 + k_3 + \Sigma k_4^i\,(M)} \text{ (neglecting 9)} \qquad (12)$$

where the summation $\Sigma k_4^i(M)$ must be carried out over the i kinds of molecules M capable of entering into 4. I_p = number of molecules which phosphoresce per ml. per second, I_f = number of molecules which fluoresce per ml. per second, I_a is the number of quanta absorbed per ml. per second and ϕ is the number of molecules which dissociate per quantum absorbed.

At 4358 Å., where essentially Y_n is the same as Y_0, k_2 is about zero, k_3 is unknown but probably small and to account for the facts there must be internal conversion to the ground state from either Y_0 or from Z_0 or both. Hence we must write

$$Y_0 = X \qquad (13)$$

$$Z_0 = X \qquad (14)$$

The natural life of an upper state may be estimated from the absorption coefficients. This would be $1/k_7$. The actual mean life of molecules in the state Y_0 will be $1/(k_5 + k_7 + k_{13})$.

The following facts are available.

(1) I_p/I_a = quantum yield of phosphorescence (green) = 0.15.[22]

(2) I_p/I_f = 60 = ratio of phosphorescence to fluorescence (present work).

(3) $1/k_7 = 10^{-5}$ sec. from absorption coefficients.[23]

(4) Measured life of green phosphorescence = $1/(k_8 + k_{14}) = 1.5 \times 10^{-3}$ sec.[18]

Hence by dividing 10 by 11

$$I_p/I_f = k_5k_8/k_7(k_8 + k_{14}) = 60 = \gamma \qquad (15)$$

At 4358 Å. $(k_2 + k_3) = 0$ and therefore

$$1/(k_5 + k_7 + k_{13}) = 0.15/60\ k_7 = 2.5 \times 10^{-8} \text{ sec.} \qquad (16)$$

This is the mean life of the blue fluorescence. (Eq. 16 is derived from eq. 10.)

If $k_7 + k_5 >> k_{13}$ (*i.e.*, if internal conversion from Y_0 is negligible) one obtains from 15 and 16 the following values: $k_5 = 4 \times 10^7$ sec.$^{-1}$, $k_8 = 10^2$ sec.$^{-1}$, $k_{14} = 5.7 \times 10^2$ sec.$^{-1}$, $k_7 = 10^5$ sec.$^{-1}$. Thus the natural life of the phosphorescence would

---

(20) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

(21) W. E. Kaskan and A. B. F. Duncan, *ibid.*, **18**, 427 (1950).

(22) G. M. Almy and P. R. Gillette, *ibid.*, **11**, 188 (1943).

(23) G. M. Almy and S. Anderson, *ibid.*, **8**, 805 (1940).

be $1/k_8 = 10^{-2}$ sec. which is somewhat longer than the observed value.[20]

On the other hand one might assume $k_{14} << k_8$ and obtain $k_5 = 6 \times 10^6$, $k_7 = 10^5$, $k_{13} = 3.4 \times 10^7$, $k_8 = 6.7 \times 10^2$ all in sec.$^{-1}$. The natural life of the phosphorescence agrees with the found value in this case but k_5 and k_{13} may not be determined independently. It would be interesting to check the mean life of the fluorescence which is predicted to be 2.5×10^{-8} sec. but this value lies in a region where experimentation would be difficult.

If attention is now directed to behavior at 3650 Å., the complete expressions 10, 11 and 12 must be used. Some ratios of constants have been obtained from photochemical work[18] at 26°. Thus $k_3/k_2 = 15$, $k_4/k_2 = 2.9 \times 10^{-17}$ ml./molecule. If a mean collision diameter of 5×10^{-8} cm. is assumed for 4 and it is further assumed that 4 goes on every collision (zero activation energy, unit steric factor) one can calculate $k_2 = 3.5 \times 10^6$ sec.$^{-1}$. Hence k_3 is 5×10^7 sec.$^{-1}$. Thus if the mechanism is correct internal conversion from high vibration levels of Y must compete with loss of vibration energy by collision under conditions of this experimental work.

If Q_{4358} is the quantum yield of the green phosphorescence at 26° at 4358 Å. (when $k_2 + k_3 = 0$), Q_{3650} is the quantum yield of the phosphorescence at 3650 Å. and ϕ_{3650} is the primary photochemical yield at 3650 Å. (equation 12) one can show that

$$Q_{3650} = Q_{4358}\phi_{3650}\, k_4(\mathrm{B})/k_2 \qquad (17)$$

$$Q_{3650}/\phi_{3650} = 2.5 \times 10^3\,(\mathrm{B}) \qquad (18)$$

where (B) is the concentration of biacetyl in moles per liter. The experimentally determined slope[18] is 1.6×10^3 and the agreement with 18 is very satisfactory. Thus if the mechanism is assumed to be correct, the photochemical and fluorescence yields are certainly of the correct order of magnitude.

If attention is now directed to the acetone sensitized emission of biacetyl the following facts have been ascertained: (a) both the green and the blue emissions of biacetyl are sensitized by acetone; (b) the arbitrary intensity ratios of green to blue are greater for this sensitized emission than for emission by biacetyl which has absorbed either 4358 or 3650 Å. radiation. Exact calculation of the integrated intensity ratio is not possible because there is blue emission from both the acetone and the biacetyl. Approximate values for this ratio are 150:1 (22 mm. biacetyl, 106 mm. acetone), 108:1 (32 mm. biacetyl, 53 mm. acetone) both at 26° and with 3130 Å. radiation. The ratio is about 60:1 in pure biacetyl. It is concluded, therefore, that phosphorescence emission is preferentially excited by the acetone; (c) at 150° emission from the short lived state of acetone is partly replaced by biacetyl fluorescence. Luckey[16] has shown already that biacetyl suppresses the long lived emission from acetone.

The mean life of the fluorescing state of acetone (Y_0^A) is not known but presumably is much shorter than the mean life of the phosphorescing state (Z_0^A). At room temperature emission from Z_0^A is much more intense than emission from Y_0^A but the ratio is not exactly known because the two emissions overlap. As a rough estimate the ratio is about 5:1.[24] If one assumes 10^{-6} sec. as the mean life of Y_0^A and the measured value[21] of 2×10^{-4} sec. for Z_0^A, one can see that the ratio of concentrations $(\mathrm{Z}_0^\mathrm{A})/(\mathrm{Y}_0^\mathrm{A})$ is about 10^3. If the probability of energy transfer to biacetyl per collision is the same for Z_0^A as it is for Y_0^A, it is evident that most of the excitation of the biacetyl will arise from collisions with Z_0^A. This will be even more true if the life of Y_0^A is as low as 10^{-8} sec. and only slightly less true if the maximum life is used. This maximum is 10^{-5} sec. since a longer life could have been determined by Groh.[25]

A detailed mechanism involving the various states of acetone and of biacetyl could be suggested but the data are neither extensive enough nor accurate enough to warrant a detailed treatment. If the Wigner Spin Conservation Rule[26] governs the probability of energy transfer one would expect the following processes to predominate

$$\mathrm{Y}_0^\mathrm{A} + \mathrm{X}_0^\mathrm{B} = \mathrm{Y}_n^\mathrm{B} + \mathrm{X}_m^\mathrm{A}$$

$$\mathrm{Z}_0^\mathrm{A} + \mathrm{X}_0^\mathrm{B} = \mathrm{Z}_n^\mathrm{B} + \mathrm{X}_m^\mathrm{A}$$

where the superscripts A and B refer to acetone and biacetyl, respectively. In other words a molecule of acetone in the singlet upper state would be expected to excite a molecule of biacetyl to the singlet upper state by a collision of the second kind and a molecule of acetone in the triplet upper state would be expected to excite a molecule of biacetyl to the triplet upper state.

If acetone molecules in the triplet state (Z_0^A) have a very much higher concentration than those in the singlet state (Y_0^A) one would expect a very much greater excitation of biacetyl phosphorescence than of biacetyl fluorescence. Actually the ratio of green to blue is only about three times as great when excited by acetone as it is when biacetyl absorbs radiation itself. This increase is so slight that one may not at this time draw positive conclusions about the applicability of the Wigner Spin Conservation Rule to collisions between acetone and biacetyl molecules.

The authors wish to thank the various members of the research group at the University of Rochester and in particular Dr. G. B. Porter for many helpful discussions. Our gratitude is also due to Dr. George W. Luckey of Eastman Kodak Company for help in obtaining photographic plates and optical wedges as well as for helpful discussions.

ROCHESTER, NEW YORK

---

[24] R. E. Hunt and W. A. Noyes, Jr., THIS JOURNAL, **70**, 467 (1948).

[25] H. J. Groh, Ph.D. Thesis, University of Rochester, 1952.

[26] E. Wigner, *Göttinger Nacht.*, 375 (1927).