[CONTRIBUTION FROM THE AERONAUTICAL RESEARCH LABORATORIES, WRIGHT-PATTERSON AIR FORCE BASE, OHIO]

The Selective Sensitization of Biacetyl Triplet State in the Vapor Phase

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The phosphorescence of biacetyl vapor was sensitized by benzophenone at λ2750 Å. and 109°. The mechanism proposed is analogous to that used for singlet–singlet sensitization in fluid solutions when the latter is diffusion controlled. An estimate is made of the lifetime of the vapor phase phosphorescence of benzophenone ($>1.4 \times 10^{-5}$ sec.), assuming short range interaction.

Introduction

Despite the numerous references on the subject of sensitization of the luminescence of complex molecules in the vapor phase,[1–8] few systems have been studied quantitatively to any extent.[4,5,7] Of these, only the benzene-sensitized fluorescence of β-naphthylamine[4] and the benzene-sensitized fluorescence of anthracene[5] are not obscured by simultaneous photodecompositions, although the former system is complicated by effects due to vibrational stabilization of the acceptor molecule.

A fraction of donor molecules excited to the first allowed singlet state will usually end up as triplet state donors by virtue of inter-system crossing. The excited donor molecules in either a singlet or a triplet state may transfer their electronic energy to a singlet or a triplet state of an acceptor molecule provided that the energy of the donor is higher than the energy of the excited acceptor and that the over-all spin angular momentum is conserved during the transfer process. It is of interest to study pure triplet-triplet transfer not only because of the

$$^3D^* + {}^1A \longrightarrow {}^1D + {}^3A^* \qquad (1)$$

general importance of energy transfer to many areas such as photosynthesis, scintillation, radiation protection and photochromism, but because it may eventually permit selective studies of the photochemistry of triplet states without the intermediary of the singlet. In eq. 1, the asterisk denotes an electronically excited state.

This paper describes recent data on the sensitization of the vapor phase phosphorescence of biacetyl by benzophenone at 109° and λ 2750 Å.

Experimental

Materials.—Biacetyl was obtained from Matheson Coleman and Bell (m.p. −5 to −3°). This material was further purified by fractionation, the middle third fraction being retained for the experiment. The biacetyl was stored in the dark at the temperature of an alcohol–solid carbon dioxide trap and isolated from the system by a Hoke 413 packless vacuum valve.

The benzophenone was also obtained from Matheson Coleman and Bell (m.p. 48–49°). This material was used without further treatment. Its purity was checked by observation of its phosphorescence spectrum in EPA at liquid nitrogen temperature (see Fig. 1).

Apparatus.—The apparatus used was a modification of the Aminco-Keirs Spectrophosphorimeter. This instrument consists of a 150 watt Osram xenon lamp with a d.c. ballast, a grating monochromator for selection of the excitation wave length, and a grating monochromator for analysis of the luminescence beam. The luminescence is detected at 90° with a 1P21 photomultiplier, amplified and plotted against wave length with an Electro-Instrument X-Y recorder. The rotating shutter and accessories in the cell compartment (when the instrument is used as a phosphorimeter) were removed to make way for a 2 × 2 × 2 cm. quartz cell held in a brass block heated in the usual way by Nichrome wire and insulated with asbestos. Figure 2 is a schematic representation of the experimental arrangement. Valve V_1 isolating the benzophenone supply from the cell was necessary because of the low melting point of benzophenone and the high solubility of biacetyl in melted benzophenone. The cell temperature, the temperature of the benzophenone supply, the temperature of the small finger as well as the temperatures at the valves and at certain other critical points were monitored with iron–constantan thermocouples and a Leeds and Northrup precision portable potentiometer. The voltages to the Nichrome elements heating the various portions of the system were stabilized using a Stabiline 1E5102R voltage regulator.

Procedure.—The cell C, line L small finger CF, valves V_1 and V_2 were all heated to the temperature of the experiment. The benzophenone supply Bz was heated to the temperature giving the desired vapor pressure. A tracing was made with the empty cell to obtain a correction for a small amount of quartz emission. V_1 was opened and a tracing was made of the benzophenone emission. V_1 was closed and the small finger CF was frozen with liquid nitrogen. CF was then allowed to warm up to room temperature and V_2 was opened to allow biacetyl at a pressure indicated on M to flow into the heated system. V_2 was closed and a tracing was made of biacetyl luminescence in the absence of donor (the benzophenone is condensed in CF). The small finger CF was brought to the temperature of the system and after allowing one hour for mixing, a tracing was made of the luminescence of the mixture. For the next data points all gases were pumped out and the procedure was repeated with a change in either the biacetyl or benzophenone pressures.

Results

Figure 1 shows the emission spectrum of benzophenone vapor at 170°. This curve has been corrected for instrumental factors using the quinine sulfate method.[9] On the same diagram, one sees the emission of benzophenone in EPA at liquid nitrogen temperature, which was used as a criterion of purity. This spectrum agrees with that reported by Lewis and Kasha.[10] Although the vapor phase emission band of benzophenone near λ 5200 Å. coincides with the phosphorescence maximum of biacetyl, this poses no problem for the sensitization measurements because of its low intensity and because it is effectively quenched by biacetyl.

Figure 3 is a typical tracing of a sensitization experiment showing the tremendous increase in

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[1] For a review of the subject, up to 1955, see A. N. Terenin and V. L. Ermolaev, *Uspekhi Fiz. Nauk*, **58**, 37 (1956).

[2] H. Okabe, Ph.D. Thesis, University of Rochester, 1956.

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

[4] J. T. Dubois, *J. Phys. Chem.*, **63**, 8 (1959).

[5] B. Stevens, *Faraday Soc. Disc.*, **27**, 34 (1959).

[6] D. S. Weir, N. Ishikawa, J. S. Michael, N. Padnes, C. S. Parmenter and W. A. Noyes, Jr., Paper presented at the 18th International IUPAC Congress, Montreal, August, 1961.

[7] D. S. Weir, *J. Am. Chem. Soc.*, **83**, 2629 (1961).

[8] H. Ishikawa and W. A. Noyes, Jr., *ibid.*, **84**, 1502 (1962).

[9] W. H. Melhuish, *J. Phys. Chem.*, **64**, 762 (1960).

[10] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

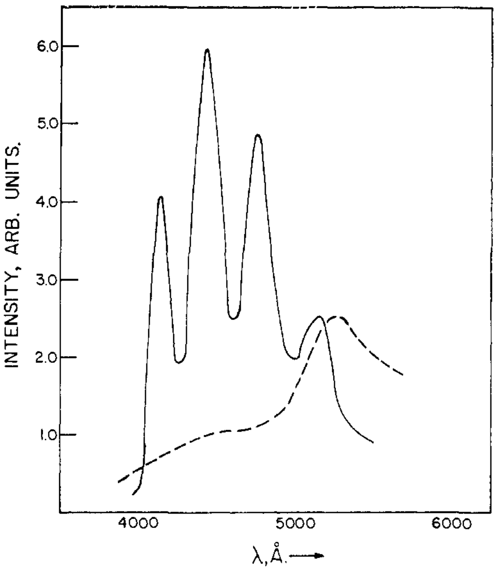

Fig. 1.—Phosphorescence of benzophenone: ———, in EPA at liquid nitrogen temperature; – – – –, vapor at 170°.

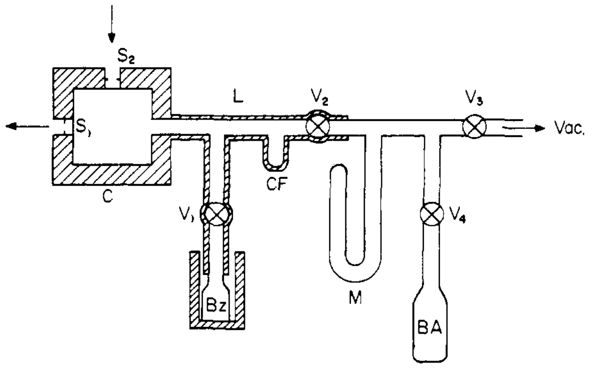

Fig. 2.—Experimental arrangement: $C = 2 \times 2 \times 2$ cm. quartz cell; S_1S_2 = slits; V_1, V_2, V_3, V_4 = Hoke 413 packless vacuum valves; Bz = benzophenone supply; BA = biacetyl supply; M = mercury manometer; L = heated line; CF = very small finger for condensation of benzophenone.

biacetyl phosphorescence with a small addition of benzophenone.

Figure 4 shows the measured ratio of phosphorescence intensity P_A of biacetyl in the presence of donor to the intensity $P_A{}^0$ in the absence of donor, as a function of donor concentration and various acceptor concentrations.

Discussion

The selective sensitization of biacetyl phosphorescence by benzophenone in fluid solutions has been demonstrated by Bäckström and Sandros.[11] This process is possible because of the very high rate of radiationless transition from the first singlet excited state to the triplet state of benzophenone. The conversion to the triplet state is essentially complete during the lifetime of the singlet state. As a result, benzophenone does not fluoresce in fluid solutions and we verified that it did not sensitize the singlet state of biacetyl in cyclohexane solutions at room temperature.

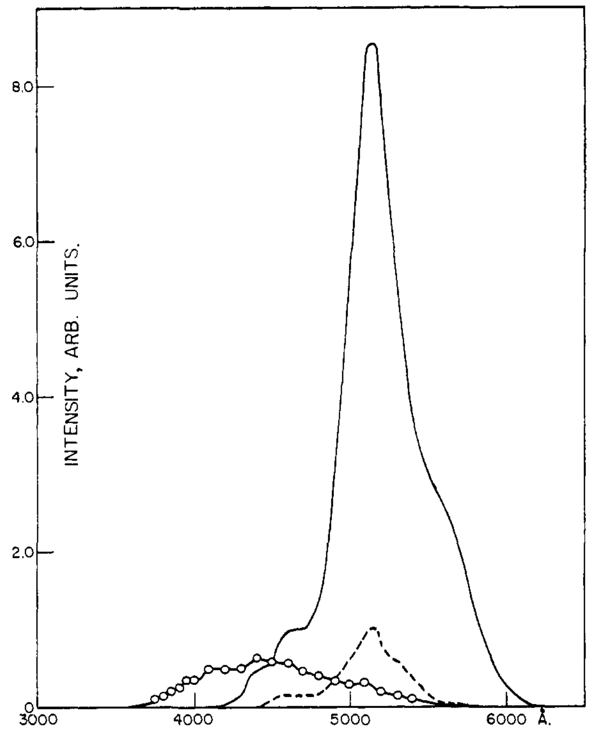

Fig. 3.—Typical tracing of sensitization experiment at λ 2750 Å.: ⊙, 0.078 mm. of benzophenone alone at 109°; – – – –, 0.22 mm. of biacetyl alone at 109°; ———, mixture of both under same conditions. This diagram is corrected for small background emission, but the spectra are not corrected for instrumental sensitivity.

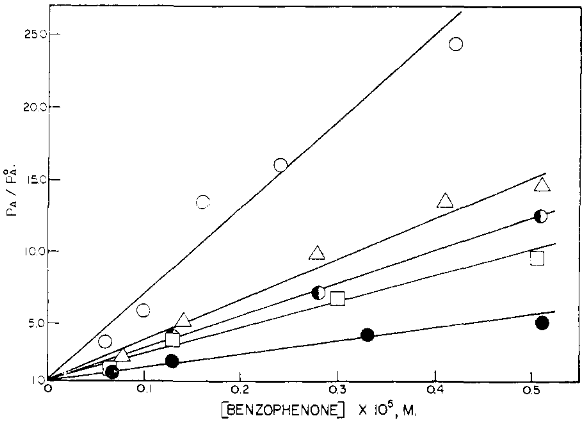

Fig. 4.—Relative increase $P_A/P_A{}^\circ$ of the phosphorescence of biacetyl in the presence of benzophenone to that in the absence of the donor. Biacetyl concentrations are: ⊙, $0.84 \times 10^{-4}\,M$; △, $2.5 \times 10^{-4}\,M$; ◐, $4.2 \times 10^{-4}\,M$; □, $5.9 \times 10^{-4}\,M$; ●, $9.2 \times 10^{-4}\,M$. The temperature is 109°, λ 2750 Å.

In the gas phase, and up to 170°, the emission of benzophenone corresponds well with the low temperature phosphorescence spectrum in EPA. With the wide slits used for the vapor phase work, the shorter wave length bands at λ 4150, 4400 and 4770 Å. were no longer resolved. These bands as well as the one at λ 5200 Å. are efficiently quenched by oxygen, and at a pressure of 0.12 mm. of benzophenone less than 2 mm. of biacetyl completely

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[11] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

quenches the emission. The following probable processes can account quantitatively for the results

$$^1\mathrm{D} + h\nu \longrightarrow {}^1\mathrm{D}^* \longrightarrow {}^3\mathrm{D}^* \qquad (2)$$

$$^3\mathrm{D}^* \longrightarrow {}^1\mathrm{D} + h\nu_{\mathrm{Dp}} \qquad (3)$$

$$^3\mathrm{D}^* \longrightarrow {}^1\mathrm{D} \qquad (4)$$

$$^3\mathrm{D}^* + {}^1\mathrm{A} \longrightarrow {}^1\mathrm{D} + {}^3\mathrm{A}^* \qquad (1)$$

$$^1\mathrm{A} + h\nu \longrightarrow {}^1\mathrm{A}^* \qquad (5)$$

$$^1\mathrm{A}^* \longrightarrow {}^1\mathrm{A} + h\nu_{\mathrm{Af}} \qquad (6)$$

$$^1\mathrm{A}^* \longrightarrow {}^3\mathrm{A}^* \qquad (7)$$

$$^3\mathrm{A}^* \longrightarrow {}^1\mathrm{A} + h\nu_{\mathrm{Ap}} \qquad (8)$$

$$^3\mathrm{A}^* \longrightarrow {}^1\mathrm{A} \qquad (9)$$

The asterisk denotes an electronically excited state. At the low concentration of acceptor used in these experiments it is reasonably assumed that the self-quenching step

$$^1\mathrm{A}^* + {}^1\mathrm{A} \longrightarrow \text{quenching}$$

is relatively unimportant. Additionally the almost linear appearance of the curves in Fig. 4 is an indication that other bimolecular processes such as

$$^3\mathrm{D}^* + {}^1\mathrm{D}$$

$$^3\mathrm{D}^* + {}^3\mathrm{D}^*$$

do not make an important contribution. These were therefore omitted from the mechanism for the sake of simplicity. Steps describing the vibrational stabilization of biacetyl triplets have also been omitted on the grounds that the addition of foreign gases at low pressures does not enhance biacetyl phosphorescence.[12]

In the experiments described, care was taken to choose conditions of incident radiation intensity, concentrations of donor and acceptor, time of exposure to light and temperature such as to avoid the difficulties that could arise due to direct photolysis of biacetyl or to the photolysis by the second-order process[13] or due to the presence of the yet unexplained product of biacetyl photolysis[12] which inhibits its phosphorescence.

Under photostationary conditions the intensity of acceptor phosphorescence p_{A} in the presence of donor is given by

$$p_{\mathrm{A}} = K_8({}^3\mathrm{A}^*) = \frac{K_8}{K_8 + K_9}\left\{\gamma_{\mathrm{x}} I_{\mathrm{A}} + \frac{K_1 I_{\mathrm{D}}({}^1\mathrm{A})}{K_3 + K_4 + K_1({}^1\mathrm{A})}\right\}$$

where γ_{x} is the yield of inter-system crossing from the first excited singlet to the triplet in the acceptor; I_{A} and I_{D} are the intensities of light absorbed by the acceptor and by the donor in the mixture. In the absence of donor, the intensity of acceptor phosphorescence is given by

$$p_{\mathrm{A}}{}^0 = \gamma_{\mathrm{x}} I_{\mathrm{A}}{}^0\left(\frac{K_8}{K_8 + K_9}\right)$$

Here $I_{\mathrm{A}}{}^0$ is the light absorbed by the acceptor in the absence of donor. The recorded signal P at wave length λ is related to the total intensity of phosphorescence p at λ by

$$P(\lambda) = kQ(\lambda)p(\lambda)$$

where k is an instrumental constant determining the fraction of emitted radiation intercepted by the detector and $Q(\lambda)$ is the signal intensity per quantum at λ. The ratio of signals recorded in the presence and in the absence of donor at the same wave length is therefore

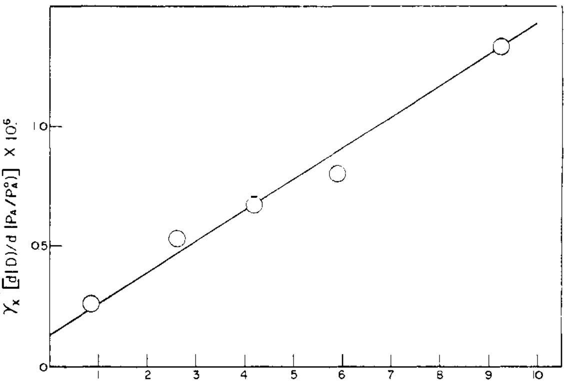

Fig. 5.—Benzophenone sensitization of biacetyl phosphorescence at 109°, λ 2750 Å.

$$\frac{P_{\mathrm{A}}}{P_{\mathrm{A}}{}^0} = \frac{p_{\mathrm{A}}}{p_{\mathrm{A}}{}^0} = \frac{I_{\mathrm{A}}}{I_{\mathrm{A}}{}^0} + \frac{I_{\mathrm{D}}}{I_{\mathrm{A}}{}^0}\left\{\frac{K_1({}^1\mathrm{A})}{K_3 + K_4 + K_1({}^1\mathrm{A})}\right\}\gamma_{\mathrm{x}}{}^{-1} \qquad (\mathrm{I})$$

Under conditions such that the extent of light absorption is a linear function of the concentrations, *i.e.*, when the first term in the expansion of the Beer–Lambert exponentials represents the absorption, eq. I becomes

$$\frac{P_{\mathrm{A}}}{P_{\mathrm{A}}{}^0} \simeq 1 + \frac{\epsilon_{\mathrm{D}}}{\epsilon_{\mathrm{A}}}\left\{\frac{K_1({}^1\mathrm{D})}{K_3 + K_4 + K_1({}^1\mathrm{A})}\right\}\gamma_{\mathrm{x}}{}^{-1} \qquad (\mathrm{II})$$

where ϵ_{D} and ϵ_{A} are the decadic molar extinction coefficients of acceptor and donor. The slopes of the sensitization diagrams are given by

$$\frac{\mathrm{d}(P_{\mathrm{A}}/P_{\mathrm{A}}{}^0)}{\mathrm{d}(\mathrm{D})} = \frac{\epsilon_{\mathrm{D}}}{\epsilon_{\mathrm{A}}}\left\{\frac{K_1\tau_{\mathrm{D}}}{1 + K_1\tau_{\mathrm{D}}({}^1\mathrm{A})}\right\}\gamma_{\mathrm{x}}{}^{-1} \qquad (\mathrm{III})$$

where $\tau_{\mathrm{D}} = 1/(K_3 + K_4)$ is the lifetime of the donor in the absence of acceptor, when donor self-quenching can be neglected, *i.e.*, low donor concentration.

The slopes of the sensitization diagrams (Fig. 4) are seen to decrease with increase in acceptor concentrations as predicted by eq. III. This behavior is completely analogous to studies of the sensitization of biacetyl by naphthalene in cyclohexane solutions[14] and to other studies in solutions[15] using phenanthrene, chrysene and diethyl ketone as donors with biacetyl as acceptor. In these studies in fluid solutions, care was taken to avoid overlap of the fluorescence of the excited donor with the absorption region of the acceptor and the rates of transfer were found to be controlled by the rates of diffusion.

From eq. III, the inverse of the product of the slopes of the sensitization curves times γ_{x} when plotted against acceptor concentration, should give a straight line with a slope equal to the ratio of the extinction coefficients of acceptor and donor, and the ratio of the slope to the intercept provides the sensitizing constant $K_{\mathrm{S}} = K_1\tau_{\mathrm{D}}$.

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[12] D. S. Weir, *J. Chem. Phys.*, **36**, 1113 (1962).

[13] W. A. Noyes, Jr., W. A. Mulac and M. S. Matheson, *ibid.*, **36**, 880 (1962).

[14] J. T. Dubois and B. Stevens, "Luminescence of Organic and Inorganic Materials," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 115.

[15] These results by M. Cox and J. T. Dubois to be submitted for publication.

γ_x for biacetyl excited near the 0–0 transition is roughly unity.[16] At shorter wave lengths such as used here it decreases to the extent that photodecomposition from the $\mathrm{II}'\mathrm{A_u}$ state (which must be initially formed) and from the first singlet excited state becomes important. Assuming no internal conversion to the ground state and noting that at short wave lengths biacetyl does not fluoresce, then $\gamma_x \cong 1 - \phi$, where ϕ is the quantum yield of the primary process. As an estimate for ϕ for the conditions of our experiment the value of 0.34 reported by Bell and Blacet[17] at λ 2650 and 100° was used. With γ_x computed in this fashion, Fig. 5 shows a test of eq. III. The results are $\epsilon_D/\epsilon_A = 770 \pm 80$ and $K_1\tau_D = 10{,}000 \pm 1000$. We did not measure ϵ_D/ϵ_A for benzophenone and for biacetyl in the vapor phase at λ2750 A. and t = 109°, but this result appears reasonable. In solutions, $\epsilon_D/\epsilon_A \simeq 600$ at that wave length.

If the transfer of energy takes place on every collision

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

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

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

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

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

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

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

The Vapor Phase Fluorescence and its Relationship to the Photolysis of Propionaldehyde and the Butyraldehydes[1]

BY R. P. BORKOWSKI[2] AND P. AUSLOOS

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The effects of pressure, temperature and wave length on the fluorescence of *n*-butyraldehyde and isobutyraldehyde have been investigated. At 3340 Å. the fluorescence yield decreases slightly with increase in pressure, while at shorter wave lengths this trend is reversed. Similar observations were made in the case of C_2H_5CHO and C_2F_5CHO. An increase in temperature reduces the relative fluorescence yields at all wave lengths. Although no phosphorescence was observed, addition of biacetyl leads to a strong emission which could be ascribed to triplet excited biacetyl formed in the energy transfer reaction: $A^3 + B \rightarrow A + B^3$ (I). The importance of this process is strongly dependent on wave length and pressure. The analysis of the products formed in the photolysis of *n*-butyraldehyde and *n*-butyraldehyde–biacetyl mixtures indicated that at 3340 Å. the intramolecular rearrangement process, $n\text{-}C_3H_7CHO + h\nu \rightarrow C_2H_4 + CH_3CHO$ (II), is strongly inhibited by biacetyl. The efficiency of this quenching process parallels that of process I. On the basis of these observations it is concluded that at 3340 Å. process II occurs from a triplet excited state.

Introduction

Although the photochemistry of the simpler aliphatic aldehydes is now fairly well established,[3] very little information is available in the literature of the emission characteristics of C_2H_5CHO, C_2F_5CHO, $n\text{-}C_3H_7CHO$ and $i\text{-}C_3H_7CHO$. The present work was undertaken in order to obtain information about the fluorescence of these compounds as a function of temperature, pressure and wave length, and to correlate these data with the photochemical observations.

Experimental

The propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were obtained from Eastman Kodak Co. and were purified on a spinning band distillation column. Only those fractions were used which were shown to be pure on a gas-liquid chromatograph equipped with a flame ionization detector. Acetone (Spectrograde), acetaldehyde and biacetyl were also obtained from Eastman Kodak Co. and used without further purification. Anhydrous pentafluoropropionaldehyde was obtained from Merck and Co. and used without any further purification. All of these compounds were thoroughly degassed and stored at −80°. The oxygen was assayed reagent grade and was obtained from the Air Reduction Co.

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

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

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

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

[2] National Academy of Sciences–National Research Council Post-doctoral Research Associate 1962–1963.

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