

tion. The great similarity of the spectra of thioamides and selenoamides show that this can not be the case. Spectroscopically the thioamides behave as if they had the structure $\bar{S}-C=\overset{+}{N}<$ and not the structure $S=C-N<$.

The strong band in the 1500–1600 cm^{-1} range which has been called the "Amide II band of thioamides" or the "Thioureide band" is comparable with the "Amide I band" of amides and not with the "Amide II band", the difference being that the stretching of the $>N-C=O$ grouping has predominantly C=O character whereas the vibration of the $>N-C=S$ grouping has predominantly C=N character. Accordingly this band occurs in the spectra of both primary, secondary and tertiary thioamides. It has been asserted that this band is missing in the spectra of primary thioamides, but this is actually not the case; it may, however, be found at frequencies as low as 1400 cm^{-1} .

The details of this investigation will be published in some forthcoming papers in this journal.

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The Relative Yields of Fluorescence and Phosphorescence of Biacetyl in Fluid Solutions

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In a previous paper¹ from this laboratory a calculation was presented indicating a quantum yield of 0.22% for the fluorescence of biacetyl in benzene solution at 20°C. This calculation was based on, *inter alia*, a value of 100 μsec for the phosphorescence mean life of biacetyl in a 0.22 M solution. Other determinations of the phosphorescence lifetime in similar solutions have occasionally yielded considerably higher values. It has also been found that prolonged irradiation of a biacetyl solution may lead to a marked increase in the phosphorescence lifetime, presumably

owing to the removal of a quenching impurity in a photochemical reaction. In the experiments reported in the present communication, the phosphorescence mean life was determined both before and after the determination of the ratio between the quantum efficiencies of fluorescence and phosphorescence.

The experimental equipment was essentially the same as earlier^{1,2}. The excitation light used was the more strongly absorbed Hg-lines at 405–408 $m\mu$ instead of the lines at 365–366 $m\mu$, which enabled us to study more dilute solutions with less reabsorption of fluorescence. The measured ratio of fluorescence to phosphorescence was varied by adding varying amounts of isopropanol, which quenches the phosphorescence probably without measurably affecting the fluorescence. In all experiments the phosphorescence lifetime (τ) was found to be constant within limits of error before and after the determination of the ratio between the quantum efficiencies of fluorescence and phosphorescence (Φ_F/Φ_P).

The results are summarized in Table 1. With increasing isopropanol concentration there is a small blue shift of the fluorescence spectrum and an increase in the value of the phosphorescence quenching constant for isopropanol. However, the gradual change of solvent seems to have a negligible effect on the value of $\tau \times \Phi_F/\Phi_P$. There is no trend in these values, although τ varied by a factor of more than 20. The mean is 23.3 μsec . This constant may be interpreted on the basis of the tentative transition diagram shown in Fig. 1. Upon excitation to a singlet excited state the molecule may either return to the ground state, emitting fluorescence (f), or undergo intersystem crossing to a triplet state (x). From this state the molecule may return to the ground state by emission of phos-

Table 1. Phosphorescence mean life and ratio of fluorescence to phosphorescence quantum yields of biacetyl in benzene and benzene-isopropanol solutions.

Conc. of biacetyl m M	Conc. of isopropanol M	τ μsec	Φ_F/Φ_P $\times 10^2$	$\tau \times \Phi_F/\Phi_P$ μsec
13.5	—	826	2.66	22.0
15.8	—	653	3.31	21.6
12.4	2.89	124	21.0	26.0
10.8	4.04	67	30.5	20.4
12.9	6.05	39	68.5	26.7

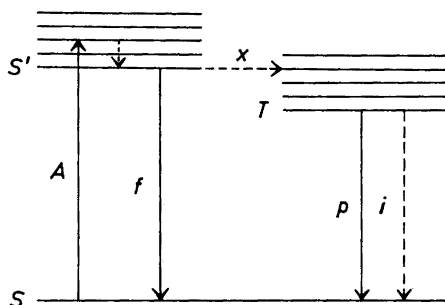


Fig. 1. Intramolecular processes in biacetyl in fluid solutions. *A* refers to absorption of light (405–408 $m\mu$). For further explanation see text.

phorescence (p) or by internal conversion (i). In fluid solutions, molecules in this state can also undergo bimolecular quenching processes ($k[Q]$). This scheme leads to the following relations:

$$\Phi_F = \frac{f}{f+x}$$

$$\Phi_P = \frac{p}{p+i+k[Q]} \cdot \frac{x}{f+x}$$

$$\tau_o = \frac{1}{p} \text{ and } \tau = \frac{1}{p+i+k[Q]}$$

$$\text{Hence } \frac{\Phi_F}{\Phi_P} \cdot \frac{\tau}{\tau_o} = \frac{f}{x}$$

From the earlier experiments¹ it can be calculated that $\tau \times \Phi_F/\Phi_P = 5 \mu\text{sec}$. The value of the phosphorescence lifetime, 100 μsec , was determined before the irradiation of the solution. A comparison with the present results indicates that, during the determination of the luminescence spectrum, the lifetime increased to almost 500 μsec . Lifetimes of more than 800 μsec have been observed on prolonged irradiation of similar solutions.

The integrated intensity ratio of fluorescence to phosphorescence in biacetyl vapour at 26°C has been estimated at $1:58.4 \pm 2.5$ by Okabe and Noyes³. Recalculated to relative numbers of quanta the ratio becomes 1:64. The phosphorescence lifetime in biacetyl vapour at 25°C has been reported as 1800 μsec by Kaskan and Duncan⁴. Thus, $\tau \times \Phi_F/\Phi_P = 28.1 \mu\text{sec}$. It is not possible to determine whether the difference between this value and that in solution, 23.3 μsec , is significant.

In the previous calculation of the fluorescence quantum yield the natural lifetime of the triplet state (τ_o) was assumed equal to the phosphorescence lifetime, 2.25×10^{-3} sec, in a solid solution at 77°K⁵. To explain the low phosphorescence quantum yield in biacetyl vapour, 0.145 ± 0.030 ⁶, a radiationless conversion to the ground state was assumed to occur directly from those vibrational levels of the triplet state that are populated in the intersystem crossing process. Porter⁷ has later published results on the photochemical reaction of biacetyl-oxygen mixtures irradiated at 436 $m\mu$. These indicate that also in the vapour state biacetyl triplet molecules in thermal equilibrium with the surroundings are formed with almost unit efficiency. On this basis the natural lifetime can be calculated at $1.80 \times 10^{-3}/0.145 = 1.24 \times 10^{-2}$ sec. From this figure $f/x = 1.9 \times 10^{-3}$ is obtained in fluid solution.

The almost equal values of the phosphorescence lifetime in a solid solution at 77°K and in the vapour state compared to the calculated natural lifetime of the triplet state indicate an internal conversion to the ground state with no or only a small activation energy. Besides this process, measurements in the gaseous state at higher temperatures^{8,9} point to other radiationless processes involving considerable activation energy.

We plan to measure quantum yields of biacetyl phosphorescence in fluid solutions, which are of primary importance for a better establishment of proposed processes.

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