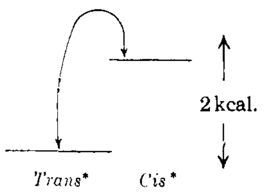
cooling much more than φ_c implies that the barrier for the *cis** → *trans** conversion is lower than that for the *trans** → *cis** conversion, indicating that the excited level of the *cis* isomer is higher than that of the *trans* isomer. This parallels the situation at the ground level, where the enthalpy difference between the two isomers amounts to 10 kcal./mole for azobenzene.[9]

A semiquantitative approach is possible, if one makes the oversimplified assumption that the variation of φ_t/φ_c with temperature is due solely to variations in φ_t. The values of φ_t/φ_c, such as those given in Table II, may then be assumed to be proportional to the rates of the *trans* → *cis* photoconversion.[10] Application of the Arrhenius equation to these rates at various temperatures leads to values for the activation energy, or potential barrier, for the thermal *trans** → *cis** conversion. Such crude calculations, based on the data of Table II, give about 2 kcal./mole for 2,2′-azonaphthalene in methylcyclohexane.

The mechanism of photoconversion emerging from the above discussion is shown in the following scheme of the electronic excited levels. The experimental evidence does not allow more far-reaching conclusions and does not exclude the possibility that other, long-lived states may serve as intermediaries between the short-lived excited singlet states. It should also be borne in mind that one may expect large quantitative variations of the described temperature effect with the nature of the compound undergoing isomerization.



The above conclusions might be compared with those reached by Schulte-Frohlinde[11] regarding the $cis \rightleftarrows trans$ photoisomerization of *p*-methoxy-*p*′-nitrostilbene with light at 365 mμ. He observed that the above photoequilibrium varies strongly with the nature of the solvent used, due to the fact that the solvent has a pronounced effect on the quantum yield of the reverse process. Schulte-Frohlinde suggests that photoisomerization involves passage through a triplet state formed from the excited singlet *cis** and *trans** states. The triplet is sterically much more similar to the *cis** state and therefore is formed from it with greater ease than from the *trans** state. This should make the *trans** → triplet → *cis** conversion more sensitive to environmental effects than the *cis** → triplet → *trans** conversion.

[9] R. J. Corruccini and E. C. Gilbert, THIS JOURNAL, **61**, 2925 (1939).

[10] This is approximately true when the rate of *trans** → *cis** is small compared with that of *trans** → *trans*. Such is the case in the range of temperatures where $\varphi_t << 1$.

[11] D. Schulte-Frohlinde, *Ann.*, **615**, 114 (1958).

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The Phosphorescence of Adsorbed Acriflavine[1]

BY JEROME L. ROSENBERG AND DONALD J. SHOMBERT

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A systematic study of the phosphorescence of acriflavine–silica gel adsorbates has uncovered certain systematic errors in some previous work: sample temperature may be indeterminate in high vacuum under prolonged illumination, and silica phosphorescence may cause appreciable interference unless near ultraviolet is removed from the exciting source. The phosphorescence decay of acriflavine is shown to be non-exponential and strictly first order over an exceptionally wide range of conditions. The postulate that dye–gel attachments occur with a distribution of adsorption energies is consistent with the observed non-exponentiality of triplet decay, with the effect of dye concentration on the decay rate and with the dependence of the decay rate on the wave length of excitation and of luminescence observation. There is an activation energy for populating the triplet state from the excited singlet, but an inefficient crossing from the lowest vibrational level of the excited singlet may occur. The activation energy for α-phosphorescence indicates that greater nuclear displacement occurs in the triplet than in the fluorescent singlet state. The non-radiative decay from triplet to ground has been shown to be less than three times as fast as the direct radiative transition.

Introduction

Early studies of the phosphorescence of acriflavine (3,6-diamino-10-methyl-acridinium chloride) revealed two long-lived radiative processes originating from the photo-excited dye.[2] Accepted interpretations clearly identified these two processes as arising from the same metastable electronic state.[3,4] The longer wave length component, Lewis' β-phosphorescence, represents the direct radiative transition from the metastable state, now identified as a triplet, to the ground singlet state, T → S. The shorter wave length component, Lewis' α-phosphorescence, has the same spectral character as fluorescence because it arises from a thermal activation from the triplet to the first excited singlet, T → S′, followed by the emission, S′ → S.[5] There has been a recent series of experimental and theoretical investigations into the details of dye luminescence,[6,7] prompted by an interest in the role of excited states in photo-

[1] This work was supported by the National Science Foundation under Grant NSF-G1237. The material presented here is abstracted from a dissertation presented to the University of Pittsburgh by Donald J. Shombert in partial fulfillment of the requirements for the Ph.D. degree in 1959.

[2] P. Pringsheim and H. Vogels, *J. chim. phys.*, **33**, 345 (1936).

[3] A. Jablonski, *Z. Physik*, **94**, 38 (1935).

[4] G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).

[5] M. Kasha, *Chem. Revs.*, **41**, 401 (1947).

[6] S. Kato and M. Koizumi, *Bull. Chem. Soc. Japan*, **30**, 27 (1957).

[7] B. Rosenberg, *J. Chem. Phys.*, **29**, 1108 (1958).

chemical reactions[8] and in organic semi-conductor phenomena.[9] Nevertheless there are still some questions as to the number of metastable states responsible for triplet emission in dyes, the role of the medium for the emission process, and the conditions for crossing over from one electronic state to another.

This paper reports an extensive series of experiments on the phosphorescence of acriflavine adsorbed on silica gel and of several other dye adsorbates. The experiments were carried out over a wide temperature range, from −196 to +40°. The principal phosphorescent characteristics observed were yield, mean life, intensity-time decay curve and spectral character.

Experimental

Materials.—Acriflavine and proflavine (3,6-diaminoacridine hydrochloride) were separated from the commercial mixture (Allied Chemical Corp.) by the method of Gailliot.[10] The dyes were recrystallized eight times from water and HCl.

Commercial fluorescein was used without purification.

Silica gel was prepared from Davison Chemical Co. 14–28 mesh material, with a surface area of 800 m.^{2}/g., by washing for several days with HCl, HNO_3 and water successively.

Alcoa activated alumina was used without further purification.

Preparation of Samples.—Acriflavine was adsorbed on silica gel from aqueous solutions. The adsorbates were dried and thoroughly outgassed in high vacuum at 250–300°. Sample concentrations ranged from 5×10^{-8} to 2.5×10^{-6} mole of dye per gram of silica, corresponding to fractional surface coverage in the range 0.001 to 0.05% and average distances between dye molecules of 90 to 320 Å. The most dilute samples had negligible reabsorption of α-phosphorescence at the wave lengths selected for observation.

Phosphoroscope.—The sample was incorporated into a conventional high-vacuum line. The optical arrangements allowed luminescence observation at 90° to the direction of incident light. In preliminary experiments, the sample was brought to a photostationary state and its luminescence observed following mechanical shuttering of the incident light. This scheme had to be abandoned because of excesssive heating of the evacuated sample in the 15 sec. of illumination required to reach the stationary state. Subsequently, a flash apparatus was constructed for exciting the sample without detectable heating. The light source was a Sylvania R4330 flash lamp, fired by a 32 μf condenser charged at 2300 volts. The flash, of about 200 μsec., was focused on the sample tube. The luminescent light was focused on the photocathode of a 1P21 photomultiplier tube. Optical filters, both selective and neutral density type, could be inserted either in the incident or the exit optical path. The signal from the photomultiplier was placed directly on a Du Mont Type 304 oscilloscope, operated single sweep, and the sweep trace was photographed. The tube response was linear in the operating range.

Thermostat.—A Dewar was used as the container for a liquid thermostat whose temperature was controlled by a cooling coil and a resistance heater. Liquid nitrogen was circulated through the coil for all measurements between −196° and room temperature. Bath liquids were Skellysolve F for use down to −130°, mixed pentenes for temperatures below −130° and methane for temperatures below −165°. Thermistors were used for temperature measurement and control, the Glennite wafer type for use down to −120° and Bendix–Friez Grade I type below −120°. The thermistor was incorporated into a d.c. resistance bridge, and the bridge unbalance was fed into a d.c. differential amplifier which served for both thermometry and control. Temperatures were known to within 1° and were controlled to within 0.01°.

The exhaust nitrogen coming out of the cooling coil was pumped into a dry box that enclosed the whole optical assembly. This made possible the operation of the cold bath all day without any clouding of the bath liquid or fogging of optical parts.

Programming.—An electronic sequence control unit performed, with adjustable time delays, the operations of triggering the light source and the oscilloscope sweep. The same unit was used for timing the activation of a solenoidal valve which admitted gases to the sample for studies made in another phase of this research.[11]

Results

Silica Phosphorescence.—It was necessary to avoid interference of luminescence by the silica gel itself with that of the dye. By removal of all radiation of wave length below 440 mμ from the exciting light, the interference was negligible in comparison with β-phosphorescence and was slightly bothersome in comparison with α-phosphorescence only below −100°.

Intensity–Time Curves.—The non-exponential character of acriflavine's phosphorescence, reported by Kato and Koizumi,[6] was confirmed. In our work the decay was followed over more than five "mean-lives" by doing a series of experiments with identical flashes, each experiment designed for the observation of the decay kinetics over a different one-second interval. The electronic amplification was adjusted so that each partial decay curve filled the whole oscillogram. Although non-exponential, the decay was first order with respect to triplet population. The initial flash-induced triplet population was varied over a factor of 256 by intensity control; the curves representing the time course of relative phosphorescent intensity (intensity divided by initial intensity) were identical at all intensities. The non-exponentiality was equally evident at all adsorbate concentrations studied. On the basis of these results rejection must be made of hypotheses on the origin of the non-exponentiality that depend on coöperative events requiring two or more triplet molecules, reabsorption of the luminescence or local heating. The implication of impurities also was dismissed as a result of the independence of the decay kinetics on method of dye purification. The temperature or pH of adsorption of the dye had no influence on the decay kinetics, nor did the source of the silica gel. One gel sample had less than 1% of the paramagnetic ion impurity level compared to the silica gel normally used, but the decay remained non-exponential.[12]

The non-exponentiality of all samples was just as marked for β-phosphorescence at liquid nitrogen temperature as for α-phosphorescence at room temperature. Similar results were obtained with a boric acid glass containing acriflavine, with proflavine adsorbed on silica and with fluorescein adsorbed on alumina. In no case where the luminescence was followed for over 5 seconds could the decay be fitted by the sum of two exponentials.

Table I summarizes some typical data on the extent of the non-exponentiality of acriflavine

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(8) R. Livingston, *Record Chem. Progr.* (Kresge Hooker Sci. Lib.), **16**, 13 (1955); G. Oster and A. H. Adelman, THIS JOURNAL, **78**, 913 (1956).

(9) R. C. Nelson, *J. Chem. Phys.*, **30**, 406 (1959).

(10) M. Gailliot, *Quart. J. Pharm. Pharmacol.*, **7**, 63 (1934).

(11) J. L. Rosenberg and D. J. Shombert, THIS JOURNAL, **82**, 3257 (1960).

(12) We are indebted to Dr. W. Keith Hall, of Mellon Institute, for supplying us with a sample of highly pure silica gel and for the impurity analyses reported here.

TABLE I

RELATIVE "MEAN LIVES" AT VARYING TIMES FROM FLASH

Excitation: all λ > 440 mμ. *Dye concentration: (a), (b), (c), 0.25; (d) 0.05 μmoles/g. silica. *Observation: (a), (b), (c), 500 mμ; (d) λ > 600 mμ.

Temp., °C.	Time from flash, sec. 0.5	3.5	6.5	*
20	1.0	2.3		(a)
− 40	1.0	2.0	2.1	(b)
−100	1.0	1.9	2.0	(c)
−100	1.0	2.0	2.7	(d)

TABLE II

MEAN LIFE OF PHOSPHORESCENCE AS A FUNCTION OF TEMPERATURE

Excitation: all λ > 440 mu. Observation: 500 mμ: Measured at: 0.3 sec. from flash.

Temp., °C.	Mean life, sec. Dye concn., 0.05 μmole/g.	Dye concn., 0.25 μmole/g.
40		0.15
30		.19
20	0.23	.24
10	.26	.29
0	.29	.35
−10	.33	.43
−20	.38	.51
−38	.50	.70
−57	.61	
−98	.61	.83

phosphorescence. The relative mean times are reciprocals of the slopes of the decay curves on semi-log plots, normalized to 1.0 for the first measurement on each sample. Each slope was measured on an oscillogram representing a one-second sweep, timed to cover either the first, the fourth or the seventh second of the decay.

Spectral Bands and Wave Length Effects.—The phosphorescence spectrum of acriflavine adsorbates, reported by Pringsheim and Vogels,^{2} was confirmed. At room temperature the green band (α-phosphorescence) predominates, extending from about 450 to 590 mμ. At −196° the orange band (β-phosphorescence) predominates, extending from 540 to 650 mμ. The peaks for the two bands are at approximately 520 and 590 mμ, respectively.

The decay of phosphorescence was found to be markedly dependent on the portion of the main absorption band used for excitation. In a group of experiments with serial excitation of the same sample at narrow bands centering about 500, 480 and 450 mμ, the decay was faster the longer the excitation wave length. The effect is observed in both concentrated and dilute dye samples, at all temperatures, in either the α- or β-phosphorescence.

Comparison of α- and β-Processes.—For a given sample, decay curves for the two luminescence bands are parallel to each other on a semi-log plot, as they should be if the two processes originate from the same metastable state. Slight deviations from the parallelism of the two curves occur in the first few tenths of a second of the decay period, the orange band showing a faster initial decay rate than the green.

Dye Concentration.—Under conditions where reabsorption of phosphorescence was avoided, a dependence of decay rate on adsorbate concentration was observed. The most dilute samples showed a slightly greater decay rate than the more concentrated, in either the green band or the orange band.

Temperature Dependence of Decay Constant.—It is difficult to assign a mean life to a process that is not exponential. In addition, the decay rates are dependent upon so many factors that it is difficult to decide which most nearly represent "ideal" conditions. The values presented in Table II are indicative of the manner in which the first order decay rate varies with temperature. Changing any of the conditions will result in different numbers, but whatever set of conditions is chosen, the numerical results are reproducible for that set. These values were obtained from the slopes of the semi-log plots at 0.3 second from the flash, at which time they become approximately linear. Although this particular set of data does not include measurements below −98°, observations on other samples showed that there was no change in the decay constants between −98 and −196°.

Temperature Independence of Spectral Band Shape.—Kinetic interpretations required that we know whether the fraction of a luminescence band intercepted by a color filter depended on the temperature of the luminescence. Since a monochromator was not available during this research, the problem was approached experimentally by observing the temperature dependence of the ratio of the observed luminescence signals through two filtering systems that admitted different cuts of the same band. The orange band was observed through a 620 mμ interference filter and through a cut-off filter passing all wave lengths above 600 mμ. The ratio of observed intensities through these filters was 0.40 ± 5% over the temperature range from +40 to −196°. For the green band the ratio of the observed intensities through 480 and 500 mμ interference filters was 0.30 ± 3% between −20 and −75°. Deviations occurred at both lower and higher temperatures, the low temperature anomalies undoubtedly due to silica luminescence.

These observations suggest that any of the filters used intercepted a constant fraction of the total band luminescence, at least within the intermediate temperature range. This result, together with the temperature independence of the β-phosphorescence decay constant below −100°, established the proportionality of the observed signal in the orange band at any time or temperature to the number of dye triplets at that time.

Phosphorescence Yield.—Absolute measurements of the phosphorescent yield were not made. Experimental evidence was acquired, however, for comparative and relative yield values. One important result came from a study of I_0, the observed intensity of the orange band extrapolated to zero decay time, at different temperatures. If a tungsten lamp was used for excitation to the photostationary state, I_0 was practically independent of temperature, changing by less than a factor of 2 between +20 and −196°. When the flash lamp was used for excitation, however, I_0 showed a much stronger temperature dependence, decreasing by a factor of 16 from +20 to −60°. Fig. 1 shows the flash data on a semi-log plot. The slope of the

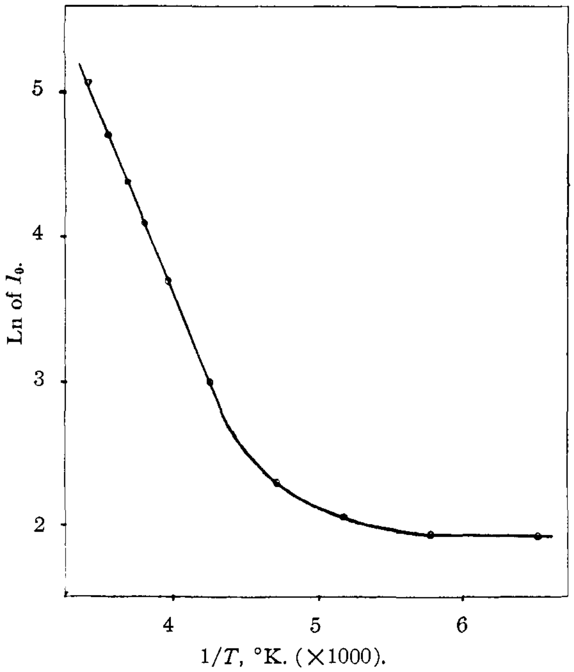

Fig. 1.—Temperature dependence of orange band intensity immediately after a flash; acriflavine concentration, 2.5 μmole/g. silica; excitation, unfiltered flash; observation, orange band above 600 mμ.

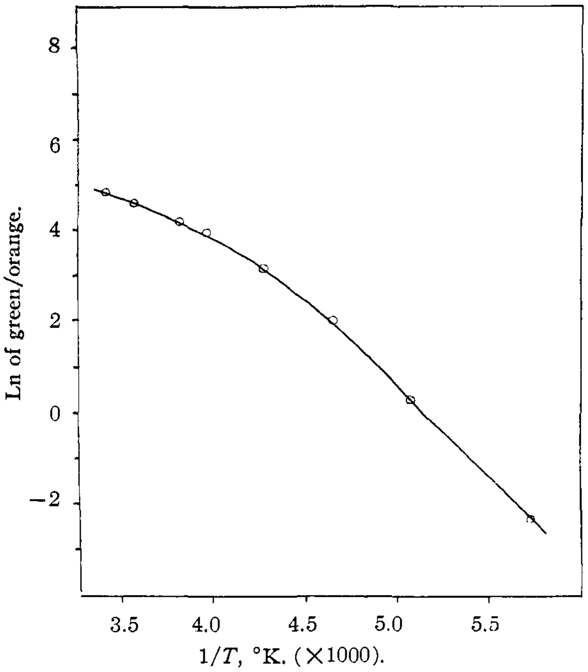

Fig. 2.—Temperature dependence of green to orange band intensity ratio; acriflavine concentration, 0.05 μmole/g. silica; excitation, flash components above 440 mμ; observation: green band, 500 mμ; orange band, above 600 mμ.

linear high-temperature portion of this curve corresponds to an apparent energy of activation of 5 kcal.

Another comparative study of interest was directed toward the relative efficiencies of β-phosphorescence at −100° as compared with α-phosphorescence at +20°. The observed integrated intensity–time curves in each case were corrected for the wave length dependent photomultiplier sensitivity and for the filter interception factors so that the data could be represented as total quantal output in each luminescence band. The outputs were normalized to a standard zero-time triplet population by dividing them by I_0 in the orange band at the respective temperatures. For a fixed flash-induced triplet population, the quantal output of α-phosphorescence at +20° was found to be 2.2 times the quantal output of β-phosphorescence at −100°.

Temperature Dependence of α- to β-Phosphorescence Intensity Ratio.—The ratios of intensity of α- to β-phosphorescence were computed as a function of temperature from measurements made over the range −98 to +20°. The values were corrected by subtracting off the observed ratio at −196°, it being assumed that the latter must represent either the tail of the green color filter or luminescence from silica. The ratios were based on intensity measurements at 0.3 second from the flash, at which point the ratios were always independent of time. The results are summarized in the semi-log plot of Fig. 2. The apparent energy of activation computed from the linear low-temperature portion of the curve is 8 kcal.

Discussion

Origin of the Luminescence Bands.—The first order character and the non-exponentiality of the decay curves are strongly suggestive that there is a manifold of metastable states from which the luminescence originates and that the luminescence is always of an intramolecular character. The fact that the deviations from exponentiality persist at −196°, where the decay rates and phosphorescence spectra are independent of temperature, refutes the hypothesis of Kato and Koizumi that several mutually accessible metastable states may exist in the same molecule.[6] A consequence of that hypothesis was that only the lowest of the available metastable states would be populated at liquid nitrogen temperature. Our inability to fit the data to a two-parameter curve is another reason for our rejecting this proposal.

We conclude that the different states are independent and assume that they are triplet states of different molecules. We propose that the multiplicity of excited energy levels is a consequence of a distribution of dye–gel interactions. The distribution could arise either from the variety of dye functional groups that might be attached to the adsorbent or from the heterogeneity of active sites on the adsorbent.

The hypothesis that not all the active sites on the silica gel are equivalent would account for a number of the experimental facts. First it would offer an explanation for the slight concentration dependence of the decay rate. In a dilute sample a higher proportion of the dye molecules would be attached to the most favorable sites than in a concentrated sample. The added hypothesis is made that the decay rate of dyes attached to the most favorable sites is slightly greater than for other points of attachment. This latter assumption is consistent with the findings of Sveshnikov and

Petrov on the solvent effect on acriflavine phosphorescence.[13] It is also not surprising that solutions of dyes in sugar and boric acid glasses yield non-exponential decays,[14] since these rigid media would be expected to have a variety of solvation positions.

The anomalous wave length effects could also be interpreted in terms of the active site hypothesis. It is well known that for $\pi-\pi^*$ transitions in conjugated molecules the wave length for the absorption peak usually shifts to the red with increasing solute–medium interaction.[15] Kato and Koizumi found a 10 mμ red-shift for the specific case of acriflavine in going from water to a silica gel adsorbate.[6] Then the dye molecules attached at the most active sites would be preferentially excited by the longer wave length components of the average absorption band and would decay more rapidly in accord with the discussion of the previous paragraph. This, in fact, was found experimentally. The slightly higher initial rate of β-phosphorescence decay as compared to α-phosphorescence can be interpreted on the same basis, if the luminescence bands are shifted in the same sense as the absorption bands. In order to avoid overlap, the β-phosphorescence always was observed on the long wave length side of the orange band's center of gravity, and the α-phosphorescence was always observed on the short wave length side of the green band's center of gravity.

Kinetics.—Although the non-uniformity of the dye molecules in their environment makes an exact kinetic analysis impossible, attention can be focussed on the properties common to all excited molecules by the use of averages. A single dye component adsorbate can be treated by considering these elementary processes.

$S + h\nu \xrightarrow{I_{\text{abs}}} S'$ (i) (Excitation)

$S' \xrightarrow{k_2} S + h\nu_{\text{green}}$ (ii) (Fluorescence)

$S' \xrightarrow{k_3} S$ (iii) (Radiationless decay from S')

$S' \xrightarrow{k_4} T$ (iv) (Populating triplet state)

$T \xrightarrow{k_5} S + h\nu_{\text{orange}}$ (v) (β-phosphorescence)

$T \xrightarrow{k_6} S'$ (vi) (Thermal activation to excited singlet)

$T \xrightarrow{k_7} S$ (vii) (Radiationless decay from T)

All of the k's are first order rate constants. For convenience of notation we shall use $k_{S'}$ and k_T, defined as

$$k_{S'} = k_2 + k_3 + k_4 \qquad (1)$$

$$k_T = k_5 + k_6 + k_7 \qquad (2)$$

Some of these rate constants are known, at least approximately, from the literature. The fluorescence lifetime of dilute acriflavine is the same in methanol solution and on polyvinyl alcohol films at room temperature. The value corresponds to 2.5×10^8 sec.$^{-1}$ for $k_{S'}$.[16,17] The similarity of the mean lives in these two cases and the absence of large differences in the absorption spectrum in various media suggest that k_2, k_3 and k_4 are separately independent of the medium, at least in the absence of heavy atoms. Ghosh and Sengupta's value for the absolute fluorescence energy efficiency of acriflavine in both water and ethyl alcohol at room temperature was recomputed to give a value of 0.53 for the fluorescence quantum yield, which would be equal to $k_2/k_{S'}$.[18,19] The radiative rate constant, k_2, is presumed to be independent of temperature, as is true for most conjugated molecules.

The observed decay constant for phosphorescence is given by

$$k_{\text{obsd}} = k_5 + k_7 + k_6(k_2 + k_3)/k_{S'} \qquad (3)$$

Below $-100°$ this becomes $(k_5 + k_7)$, which is equal numerically to 1.64 sec.$^{-1}$ from our data in Table II.

The S′ → T crossing constant, k_4, was estimated in this way. The number of triplets, T_0 formed during a short flash is given by

$$T_0 = k_4N/k_{S'} \qquad (4)$$

where N is the number of quanta absorbed during the flash. T_0 is proportional to the zero-time intensity of β-phosphorescence, I_0, the proportionality constant depending only on instrumental factors, on the shape of the emission band and on k_5, all of which are temperature independent. The number of quanta absorbed from the uniform flashes is constant because the intensity is far below the saturation level. The fluorescence decay constant, $k_{S'}$, cannot possibly be reduced by more than half its room temperature value even at $-196°$ because k_2, the radiative rate which contributes 53% to $k_{S'}$ at $+20°$, will maintain its value at the lowest temperature. Most of the observed variation in I_0 with temperature must thus be ascribed to the k_4 term. The energy of activation computed from the high temperature portion of Fig. 1, 5 kcal., must therefore be that of k_4.[20] Since the I_0 values in Fig. 1 are constant below about $-80°$, k_4 must have the form $A + Be^{-E_4/RT}$. We assume that the small temperature-independent part of k_4 corresponds either to crossings from S′ to T during the vibrational cascade following excitation or to a low probability of crossing from the lowest vibrational level of S′. The temperature-dependent part of k_4 corresponds to thermal excitation from the lowest vibrational level of S′ to a S′ → T crossing point. On the assumption that $k_3 = 0$, which implies that there is no direct thermal degradation from S′, values of k_4 and k_S can be computed separately. k_2 then has the value 1.3×10^8 sec.$^{-1}$ and k_4 ranges from 1.2×10^8 sec.$^{-1}$ at $+20°$ to 3×10^6 sec.$^{-1}$ below $-100°$. These results are perfectly consistent with the observa-

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[13] B. Ya. Sveshnikov and A. A. Petrov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 461 (1950); [*Chem. Abstracts*, **44**, 5217g (1950)].

[14] V. A. Pilipovich and B. Ya. Sveshnikov, *Doklady Akad. Nauk S.S.S.R.*, **119**, 59 (1958); [*Chem. Abstracts*, **53**, 2781d (1959)].

[15] S. Nagakura and H. Baba, THIS JOURNAL, **74**, 5693 (1952).

[16] A. Schmillen, *Z. Physik.*, **135**, 294 (1953).

[17] A. Scharmann, *Z. Naturforsch. Pt. a*, **11**, 398 (1956).

[18] S. B. Sengupta, *J. Indian Chem. Soc.*, **15**, 263 (1938).

[19] J. C. Ghosh and S. B. Sengupta, *Z. physik. Chem. B*, **41**, 117 (1938).

[20] The value for E_4, 5 kcal., would be raised by less than 1 kcal. if allowance is made for the slight temperature dependence of $k_{S'}$.

tion that I_0 is almost temperature independent if the phosphorescence is observed following a photostationary illumination with a tungsten lamp. For this condition steady-state kinetics leads to equation 5 for the triplet population

$$T_0 = k_4 I_{\text{abs}}/(k_{S'}k_T - k_4k_6) \qquad (5)$$

where I_{abs} is the quantal rate of light absorption during the photostationary state. The population of triplets is seen to be dependent on the rate both of the S′ → T process and also the reverse T → S′ process. The temperature dependence of the two just about cancel each other.

The energy of activation for α-phosphorescence, E_6, was estimated in two ways. k_6 was estimated from k_{obsd}, the reciprocal of the mean life as tabulated in Table II, by use of equation 3. k_6 ranges from 0 at $-100°$ and below, to 5.3 sec.$^{-1}$ at $+20°$. The resulting values of k_6 gave a linear semi-log *vs.* $1/T$ plot, with $E_6 = 6$ kcal. Because of errors inherent in the several subtractions required for this procedure, the following method was used. The ratio of α- to β-phosphorescence intensities at any time is proportional to $k_2k_6/k_5k_{S'}$. The proportionality constant is independent of temperature because of constant geometrical and optical factors and invariant band shapes. Also, k_2 and k_5 are independent of temperature. Thus, the plot in Fig. 2 represents the temperature dependence of $k_6/k_{S'}$. At the lower temperatures, where $k_{S'}$ is independent of temperature, the observed slope leads to a value of 8 kcal. for E_6. This method is believed to be more reliable than the use of k_6 values obtained from the decay rates. The high-temperature break in the Fig. 2 curve is attributed to the increase in $k_{S'}$ and to the slight temperature dependence of the green band shape.

The energy difference between radiation from the S′ and T states, obtained from the peak wave lengths of the bands, is about 5 kcal. The difference in activation energies for the T → S′ and S′ → T steps, $E_6 - E_4$, is 1 to 3 kcal. short of the spectroscopic difference in the levels. This is not surprising if the T state radiates to a higher vibrational level of S than does the S′ state. This would correspond to a greater nuclear displacement in the T state than in the S′ state.

Internal Conversion.—The assumption was made above that $k_3 = 0$. Semiquantitative estimates of the ratio of steady-state fluorescence to α-phosphorescence at room temperature indicate that $k_3/k_{S'}$ does not exceed 0.1. We tried to estimate the effectiveness of the direct radiationless depopulation of the triplet state, reaction vii. From the experimental comparison of the low temperature β-phosphorescence yield with the room temperature α-phosphorescence, we estimate that k_5/k_T is at least 0.25. We thus cannot exclude the participation of step (vii) in depopulating the triplet state on the basis of our data. Reactions of type (vii) occur very rapidly in fluid media. Apparently the degrees of freedom responsible for this type of quenching are not completely frozen out in adsorbates.

Triplet–Triplet Interactions.—The observed first order character of phosphorescence excludes the participation of triplet–triplet quenching of the type almost universally observed in fluid solutions. Since this type of interaction has been shown to be diffusion controlled,[21] it is not surprising that it be excluded in the rigid adsorbates studied here.

(21) H. Linschitz and K. Sarkanen, THIS JOURNAL, **80**, 4826 (1958); R. Livingston, *ibid.*, **77**, 2179 (1955).

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The Reaction of Oxygen with Electronically Excited Acriflavine[1]

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The interaction between oxygen and photo-excited acriflavine adsorbed on silica gel was studied over a wide range of conditions with the flash technique. The following elementary processes are proposed, where S and T are the ground state and first triplet state, respectively, of acriflavine, and O_2* is vibrationally excited O_2.

$$T \longrightarrow S + h\nu_{\text{phosphorescence}} \qquad \text{(v)}$$

$$T + O_2 \longrightarrow S + O_2^* \qquad \text{(viiia)}$$

$$T + O_2^* \longrightarrow \text{oxidation product} + h\nu_{\text{chemiluminescence}} \qquad \text{(ix)}$$

$$O_2^* \xrightarrow{\text{surface}} O_2 \qquad \text{(x)}$$

$$S + O_2^* \longrightarrow S + O_2 \qquad \text{(xi)}$$

From -160 to $+10°$ reaction (viiia) is collision limited and is almost independent of temperature. Below $-160°$ the rate-controlling step of (viiia) is the desorption of O_2* with an activation energy of 5 to 6 kcal. and in this range the reaction of T with O_2 competes poorly with phosphorescence (v). Practically all O_2* is deactivated by (x) or (xi). Reaction ix never utilizes more than 10% of O_2*. Reaction ix is accompanied by a good yield of chemiluminescence from the oxidation product.

Introduction

In an attempt to elucidate the mechanism of photo-oxidations sensitized by organic dyes considerable attention has been given to the effect of oxygen on dye phosphorescence. Kautsky and his associates reported that the phosphorescence in vacuum of some dyes, when adsorbed on silica or alumina gel, is quenched by very small amounts of

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