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]

BY JEROME L. ROSENBERG AND DONALD J. SHOMBERT

RECEIVED OCTOBER 5, 1959

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.

$$T \longrightarrow S + h\nu_{\text{phosphorescence}} \quad (v) \qquad\qquad T + O_2 \longrightarrow S + O_2^* \quad (viiia)$$

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

$$O_2^* \xrightarrow{\text{surface}} O_2 \quad (x) \qquad\qquad S + O_2^* \longrightarrow S + O_2 \quad (xi)$$

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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(1) Presented before the 135th National Meeting of the American Chemical Society, Boston, April 9, 1959. 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 January, 1959.

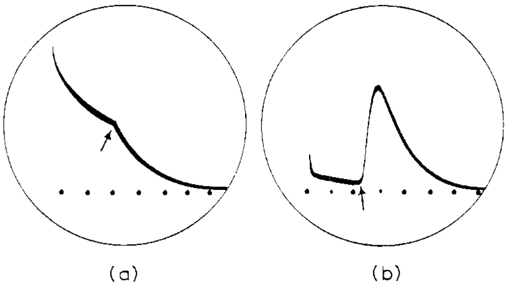

Fig. 1.—Effect of oxygen admission on acriflavine phosphorescence; dye concentration, 2.5 μmole/g. silica; excitation, unfiltered flash; temperature, −98°; oxygen pressure: zero before arrow, 0.1 mm. after arrow; observation: (a) orange band above 600 mμ; (b) green band, 500 mμ; timing marks, 0.2 sec.

oxygen.[2-4] Gases such as helium, nitrogen and hydrogen do not affect the phosphorescence. Acriflavine has been the most extensively studied dye with respect to phosphorescence quenching.[2-9] Its extreme sensitivity to oxygen led to its use as an oxygen meter by Pollack, Pringsheim and Terwoord.[10] Oxygen is not the only substance which affects the phosphorescence of acriflavine; nitric oxide, butadiene, ethylene, and other gases have also been observed to quench.[8,11]

Kautsky and Müller also observed a light-producing reaction of oxygen with the triplet state of a group of dyes.[4] They adsorbed the dye on silica or alumina gel and illuminated the gel at liquid nitrogen temperature in vacuum; under these conditions only the β-phosphorescence (radiative triplet to ground process) was visible. Then they turned off the light and admitted oxygen to the still-glowing sample. They observed a bright flash of light having the color of the dye fluorescence. The intensity of the light burst was reported to be dependent upon oxygen pressure, intensity of illumination, and the time interval between turning off the light and admitting the gas. They also stated that this reaction, which might be called a chemiluminescence, is perhaps two orders of magnitude more sensitive to oxygen than is the quenching of phosphorescence. They proposed that two triplets are involved and that an excited singlet is formed.

The application of kinetic and spectroscopic methods to these and other features of the reaction of oxygen with dye triplets is described in the present paper. The use of the flash technique supplements the work of others on photo-oxidations by photostationary state methods.[12,13]

Apparatus.—The samples studied were dye-gel adsorbates. Details of sample preparation, thermostating, timing of gas admission, illumination and luminescence observation are given in the preceding paper.[14] Most of the studies reported below were performed on acriflavine-silica gel adsorbates. The intensity of the orange luminescence band is always proportional to the number of triplets since β-phosphorescence, step v in the preceding paper, is the only process giving rise to this band. The green band, however, has a more complicated interpretation because it arises both from α-phosphorescence and from the reaction of triplets with oxygen.

Reactions between oxygen and dye triplets were carried out in three ways:

a. **Sudden Mixing.**—Oxygen was added to the sample during the dark period following a flash excitation. This procedure excluded the participation of the excited singlet state, S′, which has a very short half-life. If the orange band was observed a discontinuous increase in the decay rate of the phosphorescence marked the admission of oxygen.

$$T + O_2 \xrightarrow{k_8} X + Y^* \qquad \text{(viii)}$$

This discontinuity represents the addition of collisional oxygen-triplet processes (viii) to the strictly first order methods of triplet removal that existed in vacuum, steps v, vi and vii of ref. 14. If the green band was observed and the triplet population and oxygen pressure were sufficiently high, the admission of oxygen was marked by a sudden increase in the luminescence, Kautsky's burst, due to the onset of a chemiluminescent process. These two cases are illustrated in Fig. 1.

b. **Sudden Activation.**—The oxygen was admitted before the exciting light was flashed. The oscillogram for either band was a continuously decreasing curve, the slope of which depended on all processes, quenching and chemiluminescence, leading to triplet removal. A maximum in the time course of decay of the green band never was observed with this method since it would have occurred during the flash and would have been obscured by the intense scattering from the exciting light.

c. **Steady State.**—With continuous irradiation in the blue, the orange band could be studied during illumination.

In reaction viii above, Y* is the active intermediate for photo-oxidation. If Y* is some excited form of oxygen, then X in (viii) is identical with the dye ground state, S, and the primary step may be written as

$$T + O_2 \xrightarrow{k_8} S + O_2^* \qquad \text{(viiia)}$$

If Y* is a radical, such as HO_2, then the quenching reaction destroys dye and the product X is chemically different from acriflavine.

Results and Discussion

Dependence on Triplet Concentration.—The primary step, (viii) or (viiia), was shown to be first order in triplets by three methods, in which the orange band intensity was measured. For reactions by sudden mixing, the triplet concentration was varied by as much as a factor of 128, yet the curves obtained, by plotting (luminescence intensity/initial triplet concn.) *versus* time, were identical. The first order character of step viii was confirmed by the methods of sudden activation and of steady-state phosphorescence.

The observed intensity in the green band is more complex because it includes contributions from both α-phosphorescence and chemiluminescence. The over-all intensity in the green in the presence of oxygen was observed to be of higher-than-first order dependence on triplets but not as high as second order. This was shown by two methods. Fig. 2 shows examples of reactions by sudden mixing in which the triplet concentration at the instant of

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[2] H. Kautsky, A. Hirsch and W. Baumeister, *Ber.*, **64**, 2053 (1931).

[3] H. Kautsky and A. Hirsch, *Z. anorg. allgem. Chem.*, **222**, 126 (1935).

[4] H. Kautsky and G. O. Müller, *Z. Naturforsch.* Pt. *a*, **2**, 167 (1947).

[5] J. Franck and P. Pringsheim, *J. Chem. Phys.*, **11**, 21 (1943).

[6] S. Lipsky, Ph.D. Thesis, University of Chicago, 1954.

[7] J. J. Sjoblom, Ph.D. Thesis, University of Minnesota, 1956.

[8] S. Kato, *Bull. Chem. Soc. Japan*, **30**, 34 (1957).

[9] S. Kato, K. Kimura and M. Koizumi, *ibid.*, **30**, 38 (1957).

[10] M. Pollack, P. Pringsheim and D. Terwoord, *J. Chem. Phys.*, **12**, 295 (1944).

[11] J. Brugger, unpublished, cited in S. Lipsky, *op. cit.*, p. 23.

[12] R. Livingston and K. E. Owens, THIS JOURNAL, **78**, 3301 (1956).

[13] G. Oster, J. S. Bellin, R. W. Kimball and M. E. Schrader, *ibid.*, **81**, 5095 (1959).

[14] J. L. Rosenberg and D. J. Shombert, *ibid.*, **82**, 3252 (1960).

mixing was varied. It can be seen that the height of the pip is affected by triplet concentration; it can be made to disappear altogether by making the triplet concentration very low. Another method leading to the same conclusion was to vary the triplet concentration for reactions by sudden activation.

Since the order with respect to triplets is different for the two bands, at least two different processes must be involved. A concerted mechanism involving more than one triplet can be ruled out because of the low probability that two triplets will be close enough together to participate in a reaction simultaneously. We therefore assume a stepwise mechanism, the chemiluminescence being the second step

$$T + O_2 \xrightarrow{k_8} X + Y^* \qquad \text{(viii)}$$

$$T + Y^* \xrightarrow{k_9} Z + h\nu_{\text{chemiluminescence}} \qquad \text{(ix)}$$

Quenching of the orange band will appear to be first order in triplets if, as will be shown to be the actual case, a very small percentage of the intermediate Y* undergoes reaction ix. Chemiluminescence will be of higher-than-first order in triplets because it requires that the gaseous product of an oxygen-triplet reaction collide with a second triplet. A low chemiluminescent yield could be accounted for by deactivation of the intermediate on collision with the silica surface (x) or with a ground-state dye molecule (xi).[13]

$$Y^* \xrightarrow[\text{surface}]{k_{10}} Y \qquad \text{(x)}$$

$$Y^* + S \xrightarrow{k_{11}} Y + S \qquad \text{(xi)}$$

The concentration of the intermediate is given by

$$\frac{d[Y^*]}{dt} = k_8[O_2][T] - k_9[T][Y^*] - k_{10}[Y^*] \qquad (1)$$

[Y*] attains a maximum value shortly after a reaction is initiated. The triplet population was found not to change appreciably during the attainment of the maximum in the green burst, as can be seen by comparing the orange and green band traces in Fig. 1. Therefore the maximum intensity of chemiluminescence is given by equation 2, where ϕ is the luminescent efficiency of reaction ix.

$$I_{\text{chemiluminescence}_{\max}} = \frac{\phi k_9 k_8 [O_2][T]^2}{k_9[T] + k_{10}} \qquad (2)$$

The over-all order of chemiluminescence with respect to triplets is seen to be 1 and 2.

Efficiency of the Chemiluminescent Reaction.—An estimate of the efficiency with which the energy carrier Y* may be utilized for chemical purposes was made by estimating the fraction of Y* molecules which undergo reaction ix. This fraction was approximated by the ratio of excess integrated light intensity in the green burst to the decrease in the integrated intensity of the β-phosphorescence orange band caused by the admission of oxygen to a decaying sample in the dark. Appropriate corrections were made for instrumental and filter factors.[15] These ratios, listed in Table I for a variety of conditions, would equal the fractional efficiencies of utilization of Y* for reaction ix if the assumption is made that the quantum efficiencies for fluorescence and for chemiluminescence (ix) are the same and if radiative decay were the only fate of triplets at low temperatures in vacuum. Since the radiative efficiency of β-phosphorescence per triplet molecule may be as low as 0.25,[14] the actual probability that a Y* molecule undergoes reaction ix may be as low as 0.25 times the ratio listed in the last column of Table I. It is evident that no more than a few per cent. of all Y* molecules formed in (viii) undergo reaction ix. It can also be seen that the order of chemiluminescence with respect to triplets is between 1 and 2. The reason for the low efficiency must obviously be the deactivations of Y* represented by (x) or (xi). It can also be shown that collisions of Y* with the silica surface have a low effectiveness for deactivation or the over-all efficiency of the chemiluminescence would not be as high as it is. Our results would actually be compatible with the assumption

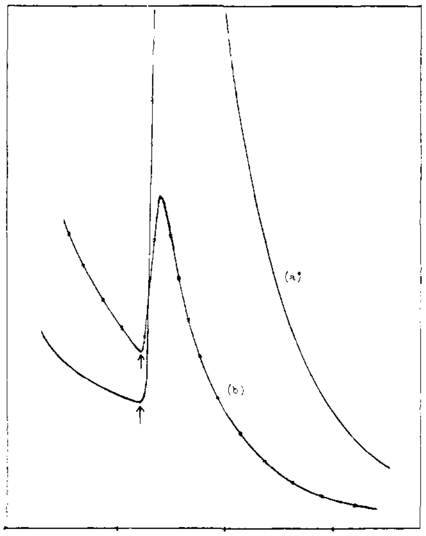

Fig. 2.—Effect of triplet concentration on chemiluminescence by method of sudden mixing; dye concentration, 0.05 μmole/g. silica; excitation, flash components above 440 mμ; temperature, −100°; observation, green band, 500 mμ; oxygen pressure: zero before arrow, 0.5 mm. after arrow; relative initial triplet concentration: (a) 64, (b) 1.

TABLE I

EFFICIENCY OF THE CHEMILUMINESCENT REACTION

Excitation: flash, all wave lengths above 440 mμ. Observation: green band, 500 mμ, orange band, all wave lengths above 600 mμ.

Temp., °C.	Oxygen press. after admiss., mm.	Relative triplet concn. at oxygen admiss.	Chemiluminescence quanta (corr.)/ Quenching loss of phosphoresc. quanta
−100	0.001	1	0.05
−100	.02	1	.08
−100	.04	1	.08
−100	.04	0.025	.01
−100	.1	1	.06
−100	.4	1	.06
−135	.1	1	.05
− 40	.1	1	.04
−100	.6	0.025	.01
−100	.6	0.003	.005

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(15) D. J. Shombert, Ph.D. Thesis, University of Pittsburgh, 1959.

that the deactivation of Y* by collision with a ground-state dye molecule (xi) has a rate constant of the same order of magnitude as that of the chemiluminescent reaction ix if silica deactivation plays no role.

Effect of Oxygen Pressure.—The rate constant for quenching by oxygen, reaction viii, can in principle be obtained by measuring the decay rate of β-phosphorescence following sudden activation. Although this method is subject to error because of the small reservoir of oxygen within a gel pore and the consequent poor buffering with respect to oxygen pressure, an order-of-magnitude value for k_8 could be obtained. In a typical experiment, at an oxygen pressure of 5×10^{-5} mm. the decay constant at $-100°$ is on the order of 6 sec.$^{-1}$. The decay constant for the same sample in vacuum was 1 sec.$^{-1}$, thus $k_8[O_2]$ is 5 sec.$^{-1}$. If a dye molecule is assumed to have an effective area of 25 Å.^{2}, about 1 collision in 10 to 20 is effective in deactivating triplets. Similar results have been obtained by Lipsky[6] and Kato.[8]

The green burst on sudden mixing was a phenomenon which required a minimum oxygen pressure, whose magnitude depended on the triplet concentration and the temperature. These complications arise in part from the slowness of passage of oxygen through the pores of the gel at the "instant" of mixing and in part from the increased interference of α-phosphorescence with the observation of chemiluminescence at higher temperatures.[14] We could not confirm Kautsky's claim that the burst could be used as a more sensitive oxygen detector than phosphorescence quenching. The smallest partial pressure of oxygen which produced a burst in our experiments was 5×10^{-5} mm.

Lipsky has reported that although phosphorescence, as measured with a rotating-disc phosphoroscope, is noticeably quenched at a very small partial pressure of oxygen, the quenching is incomplete at very high pressures when the observation was made a few milliseconds after the excitation. For the portion of the decay which we observed, 20 to 1000 milliseconds after the excitation, quenching was complete at oxygen pressures above 10^{-3} mm. Simple quenching theory predicts an increased fractional quenching with increasing time lapse after excitation, and phosphorescence quenching might well be used as an oxygen meter for oxygen pressures as low as 10^{-7} mm., by measuring intensities at longer dark times, up to 10 or 20 seconds. Another possible source of the discrepancy between this work and that of Lipsky is that the latter, observing the green band, may have observed an "anti-quenching" contribution from chemiluminescence.

Oxygen Consumption.—Kautsky and Müller reported that oxygen is consumed by acriflavine triplets.[4] In this work oxygen consumption in a sealed-off sample was demonstrated by following the change in phosphorescence quenching before and after a series of flashes. Oxygen consumption was shown to be of higher-than-first order in triplets. Although the exact number of triplets formed per flash was not known, estimates of this quantity together with measurement of the oxygen uptake led to the conclusion that no more than a few per cent. of primary oxygen-triplet quenching collisions (viii) result in oxygen consumption.[15] It appears probable that oxygen is consumed in the luminescent reaction ix, since the yields for oxygen consumption and for chemiluminescence are in the same order of magnitude. This hypothesis is supported by the fact that oxygen consumption is of higher-than-first order in triplets. Additional support comes from the study of the effect of high oxygen pressure. There is an optimum pressure above which both oxygen consumption and chemiluminescence decrease. This undoubtedly is due to the competition of O_2 (viii) with Y* (ix) for triplets.

Spectrum of Chemiluminescence.—A working hypothesis was made at the beginning of this research that the spectrum of chemiluminescence is the same as that of fluorescence and α-phosphorescence.[4] We had hoped to test this assumption by photographing the green burst through a spectrograph, but the low intensity made this experiment impossible with the equipment available to us. Instead comparisons were made of the luminescence–time curves at different portions of the green band in sudden mixing experiments. If the α-phosphorescence and the chemiluminescence have the same spectra the time curves through two filters should be superimposable if normalized at one point. This turned out not to be the case. The burst in oxygen contained relatively more light of short wave length than did the phosphorescence in vacuum. From a series of experiments of this type the chemiluminescence band was estimated to be shifted to short wave lengths by 20 to 30 mμ. The substance giving rise to this band was assumed to be an oxidation product of acriflavine. To test this hypothesis a sample of acriflavine on silica gel was illuminated in oxygen until visible discoloration had occurred. This oxidized sample was eluted and its absorption spectrum was found to have a maximum in the ultraviolet, with a secondary peak perhaps 30 mμ toward shorter wave lengths as compared with the absorption spectrum of acriflavine. The latter peak may correspond to the primary photo-oxidation product and the ultraviolet peak to a more highly oxidized material.

The spectral evidence and the results on oxygen consumption refute the proposal by Förster that the "chemiluminescent" burst merely represents α-phosphorescence stimulated thermally by the local heating caused by a simple oxygen-catalyzed $T \rightarrow S$ process (vii).[16] His proposal also seems unlikely on general considerations of heat conductivity.

Dependence on Temperature.—The quenching of β-phosphorescence is virtually independent of temperature over a very wide temperature range. The fraction of collisions effective for quenching is so high that the energy of activation for this process must be very small or zero. The chemiluminescent burst is observable over the same wide temperature range, and the quantum yield, to a first approximation, is a constant for comparable triplet concentrations. The luminescent step in

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(16) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951, p. 275.

the reaction, process ix, must thus also have an energy of activation of nearly zero.

However, at liquid nitrogen temperature there is neither quenching of the orange band nor chemiluminescence in the green band when oxygen at a pressure of 1 mm. is admitted to an excited phosphor.[17] If the dye is excited by a flash in the presence of oxygen no quenching is observable, even at a pressure of 0.05 mm. The critical temperature below which neither quenching nor chemiluminescence occurs was found to be between -160 and $-182°$. The observed transition from quenching to no quenching can be explained by assuming that the rate of reaction viiia at low temperatures is limited by the desorption of excited oxygen from the silica surface. The mean time that an adsorbed molecule spends on the surface is given by equation 3, where t_0 is the period of vibration of

$$t = t_0 e^{Q/RT} \qquad (3)$$

a molecule attached to the surface and Q is the heat of adsorption.[18,19] If the time computed for desorption is short compared with the natural lifetime of the triplet with respect to phosphorescence, then desorption is not rate-limiting. If the desorption time is large, on the other hand, the triplets will radiate their energy before Y* can remove it. The natural phosphorescent life-time of a triplet throughout the low temperature range is 1 second. From such considerations, a minimum value of 5.6 kcal. was computed for Q and t_0 for this minimum Q is about 10^{-12} second. These numbers are not in bad agreement with the known heat of adsorption of oxygen on silica and other surfaces of about 4 kcal.[19] and with order-of-magnitude expectations for the vibrational period of an adsorbed molecule.

Reactions of Other Dyes.—Reactions with oxygen by sudden mixing were performed with proflavine adsorbed on silica and with fluorescein adsorbed on alumina. The chemiluminescent reaction was observed for both of these dyes and the kinetics studied qualitatively. The general dependence on triplet concentration, temperature and oxygen pressure observed with these dyes was the same as with acriflavine. The mechanism is therefore assumed to be the same in all these reactions.

General Discussion

The luminescent reaction has been shown to consume oxygen and the chemiluminescence to arise from an oxidation product of the dye. The product Z in reaction ix is thus identified as an oxidation product of acriflavine. By a less direct method Y* and the product X in reaction viii can be identified. After 100 flashes in the presence of oxygen an appreciable fraction of the total dye molecules undergo reaction viii. If a permanent chemical change in the dye were produced by the quenching reaction, this change would have been noticeable; yet no change in the absorption spectrum was observable after hundreds of flashes in oxygen. We conclude that the quenching reaction viii does not result in chemical change of the dye.

We therefore identify Y* as excited oxygen and X as ground-state acriflavine, as in equation viiia. It is conceivable instead that Y* could be a radical, such as HO_2, and that a back-reaction could account for failure to observe a change in the dye. This requires an extraordinary coincidence, namely, that nearly all of the radicals formed in process (viii) should strike just those dye molecules which had previously undergone reaction (viii) before the radicals escape from the pores or recombine with each other. Equally implausible is the assumption that Y* is HO_2 resulting from the interaction of O_2 with water adsorbed on the silica. The energy requirement for this hydrogen abstraction reaction is not met by the 48 kcal. per mole available in the acriflavine triplet.[20]

Kautsky suggested that electronically excited oxygen was formed in the quenching reaction[4]; Lipsky thought it more probable that vibrationally excited oxygen was formed. We are inclined to the latter view. Quenching of phosphorescence by oxygen is observed for many dyes, and it is unlikely that conditions for electronic resonance transfer between the dye and oxygen could be met for so many dyes. Unfortunately no evidence has been obtained as to whether the primary oxidation product Z is a moloxide, a peroxide or some other derivative of the dye. The similarity of the luminescence bands suggests that the aromatic ring structure in Z is not very different from that in acriflavine.

Our assumption that the active oxidizing agent, Y*, is excited oxygen and not a dye peroxide or other labile dye-oxygen complex is based on its volatility. Adsorbed dyes are completely nonvolatile under our experimental conditions, as are dye peroxides. Since the oxidation reaction ix requires that Y* reach a triplet and since triplets are 1000 Å. apart on the average, the peroxide hypothesis could not account for the results. Also, the escape of Y* from the surface is required to account for the fall-off of quenching at liquid nitrogen temperature. The gaseous transfer of the oxidizing principle across space is also required to account for the auto-oxidation of leucomalachite green photosensitized by acriflavine when the leuco dye and the acriflavine were adsorbed on separate granules of silica gel.[7,21]

We are not prepared to say whether vibrationally hot oxygen is the active oxidizing agent also in analogous photochemical oxidations occurring in liquid media. Oster, *et al.*, postulated a photoperoxide as the oxidizing agent in proflavine-sensitized auto-oxidations, but they pointed out that their results are equally compatible with the excited oxygen hypothesis.[13] It is possible that the peroxide may function effectively in fluid media but that excited oxygen is the only possible route in solid-gas systems.

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[17] We interpret Kautsky's report of a burst at liquid nitrogen temperature as due to an error in temperature assignment. His evacuated sample must certainly have been heated when exposed to a carbon arc light, even though the sample was immersed in liquid nitrogen. We used flash excitation to avoid thermometric errors due to the poor heat conductivity of the sample tube.

[18] J. Frenkel, *Z. Physik*, **26**, 117 (1924).

[19] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, 1943, p. 455.

[20] N. Uri, *Chem. Revs.*, **50**, 375 (1952).

[21] H. Kautsky, H. de Bruijn, R. Neuwirth and W. Baumeister, *Ber.*, **66**, 1588 (1933).