Fluorescence of Rubrene Excited by Energy Transfer from Singlet Oxygen. Temperature Dependence and Competition with Oxidation

Sir:

Energy-pooling processes involving singlet molecular oxygen are well established.[1] Recently, Ogryzlo, *et al.*,[2] reported that a stream of $^1O_2$ caused a solution of violanthrone to fluoresce. Its singlet state being at ~45 kcal [*i.e.*, twice the energy of $O_2(^1\Delta_g)$ at 22.5 kcal], it could be excited by transfer from two $O_2(^1\Delta_g)$; indeed, the glow depends on the square of the $O_2(^1\Delta_g)$ concentration. They found evidence, however, for an intermediate step involving violanthrone triplets,[3] but did not study the effect of temperature or observe other examples of transfer from $^1O_2$ to organic fluorescers.

We report here that singlet oxygen can excite the fluorescence of rubrene (R) in solution, even though it reacts with it. With $E_S \approx 53$ kcal, 8 kcal is needed besides the energies of two $O_2(^1\Delta_g)$. This "sensitized delayed fluorescence" is found to be markedly temperature dependent.

A steady flow of 10% oxygen in helium at a total pressure of 50 Torr was pumped through a radiofrequency discharge,[4] a ring of mercuric oxide for atom removal,[5] two light traps, a Pyrex cell with outer jacket for temperature control, manometer, and traps. The gas entered the cell through an inlet opening at the bottom facing a photomultiplier and left through a reflux condenser at −78°. The concentration of $O_2(^1\Delta_g)$,[6] monitored by the intensity I_{635} of the 635-mμ emission band,[7,8] could be modified by changing the interelectrode distance. A rubrene solution[9] (5 ml) of concentration R_0 was then injected into the cell, causing an immediate increase up to several hundred fold in the light output at the wavelength of rubrene fluorescence.[7,10] Because of the bubbling of gases, the intensity recordings are very jagged, precluding better than 10% accuracy. Besides, since rubrene also gives the colorless peroxide RO_2,[11] the concentration of rubrene and consequently the luminescence rapidly decrease with time. The discharge was turned off 60 sec after injecting the solution, causing an abrupt fall of the light intensity (I). Initial and final average values of I were measured on the tracings, and the final concentration (R_f) of rubrene was determined photometrically.

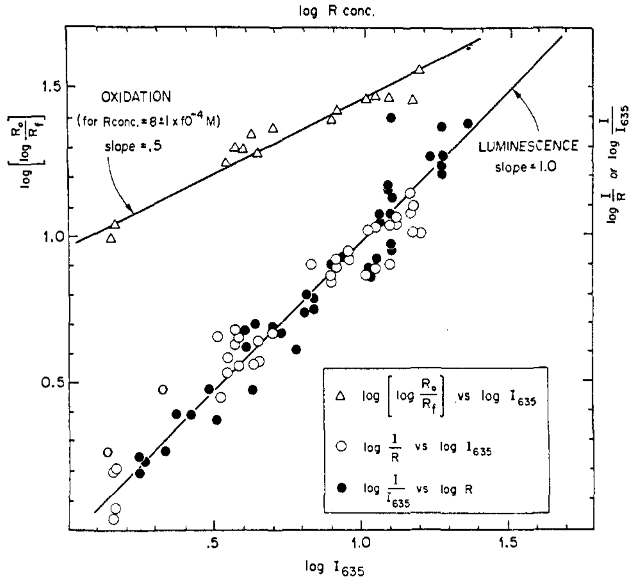

Figure 1. Effect of $^1O_2(^1\Delta_g)$ and rubrene concentration on the luminescence intensity and rate of oxidation.

Our results are compatible with the following mechanism.

$$R + {}^1O_2 \longrightarrow {}^3R + {}^3O_2 \quad (1)$$

$$^3R + {}^1O_2 \longrightarrow {}^1R^* + {}^3O_2 \quad (2)$$

$$^1R^* \longrightarrow R + h\nu \quad (3)$$

$$^3R \longrightarrow R \quad (4)$$

$$R + {}^1O_2 \longrightarrow RO_2 \quad (5)$$

Under our conditions of steady flow, the concentration of $^1O_2 \approx$ constant. By assuming steady states of ($^1R^*$) and (^3R) and $k_4 \gg k_2(^1O_2)$, one gets

$$I = k(^1O_2)^2(R) = kI_{635}(R) \quad (6)$$

whereas integration of the first-order decay of R during a standard $t = 60$ sec run gives

$$\log \frac{R_0}{R_f} = k_5(^1O_2)\frac{t}{2.3} \propto \sqrt{I_{635}} \quad (7)$$

Direct excitation of $^1R^*$ by a "dimol" $[^1O_2]_2$ would yield (6) and (7) also; see Figure 1. Our results rule out a triplet–triplet annihilation step $^3R + {}^3R \rightarrow {}^1R^* + R$ which would yield a second-order dependence of I on (R). In order for steps 1 and 2 to yield singlet excited rubrene, thermal activation must occur during reactions 1, 2, or both. Figure 2 shows the temperature dependence of the emission; the activation energy of 6.5 kcal is not unreasonable in view of the over-all energy balance. That this temperature coefficient is "genuine", *i.e.*, dependent on the energy requirement of the excitation and not on trivial experimental conditions such as viscosity, rate of flow, etc., is supported by the fact that the rate of rubrene oxidation is nearly temperature independent.

Our kinetic data do not permit a decision between a two-step excitation of $^1R^*$ with intermediate ^3R as written above, by analogy with the violanthrone mechanism,[2b] or a near-triple collision between rubrene and a short-lived "dimol" $[^1O_2]_2$. It was not possible to vary the concentration of $^3O_2$, independently of that of $^1O_2$, so Ogryzlo's criterion[3] could not be used here. But the effect of a heavy-atom solvent seem to support

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(1) See S. J. Arnold, N. Finlayson, and E. A. Ogryzlo, *J. Chem. Phys.*, **44**, 2529 (1966).

(2) (a) E. A. Ogryzlo, International Oxidation Symposium, San Francisco, Calif., Aug 1967; Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press; (b) E. A. Ogryzlo and A. E. Pearson, *J. Phys. Chem.*, **72**, 2913 (1968). A preprint is gratefully acknowledged.

(3) From the quenching effect of $^3O_2$; see footnote 2b.

(4) As in E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, **86**, 3881 (1964).

(5) R. E. Marsh, S. G. Furnival, and H. I. Schiff, *Photochem. Photobiol.*, **4**, 971 (1965).

(6) The glow of violanthrone is independent of the concentration of O_2 ($^1\Sigma_g^+$) (see footnote 2b); the same is assumed here.

(7) Through an interference filter.

(8) I_{635} is proportional to the square of the concentration of $O_2(^1\Delta_g)$; see L. W. Bader and E. A. Ogryzlo, *Discussions Faraday Soc.*, **37**, 46 (1964); S. H. Whitlow and F. D. Finlay, *Can. J. Chem.*, **45**, 2087 (1967).

(9) In *o*-dichlorobenzene, at concentrations between 4 and 16 × 10^{-4} *M*.

(10) Luminescence and fluorescence spectra agreed (peak at 580 mμ).

(11) See T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966), and references therein. RO_2 is stable at the temperatures of this work.

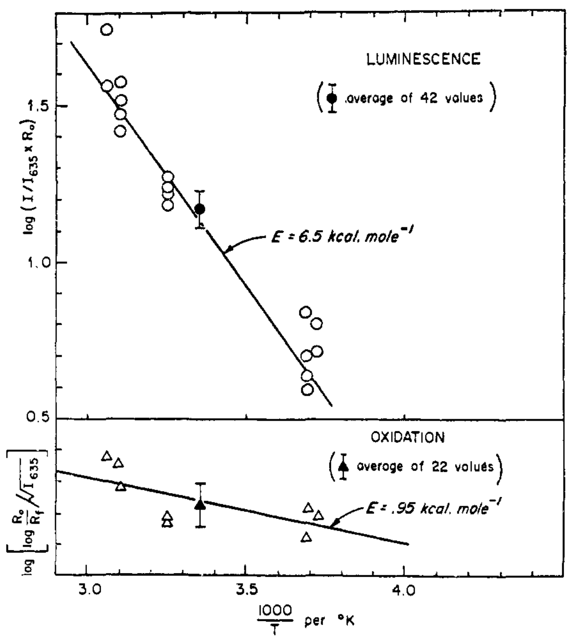

Figure 2. Temperature dependence of the light emission intensity and of the rate of rubrene oxidation.

the intermediacy of ^{3}R. Whereas the rate of oxidation and the temperature coefficient of the emission are little changed, in iodobenzene the absolute intensity is smaller by a factor of $\sim$6 than in *o*-dichlorobenzene.[12] As the oxidation is unaffected,[13] deactivation of ${}^1O_2$ cannot be invoked: when the ${}^1O_2$ quencher DABCO[14] is added to the rubrene solution, both oxidation and luminescence are drastically reduced, thus confirming the common intermediacy of ${}^1O_2$. The intensity of rubrene (photo) fluorescence does not seem influenced by the solvent either.[15] Therefore, the effect of iodobenzene seemed best explained by the deactivation of triplet rubrene by increased spin-orbital coupling due to the heavy atom. Unfortunately, the position of triplet rubrene is not known. A low triplet $\sim$22–29 kcal[16] would be compatible with its intermediacy. A high ^3R ($\sim$40 kcal[17]) would not fit with our observed activation energy, thus implying a mechanism *via* $[{}^1O_2]_2$.

Rubrene excitation (eq 1) and oxidation (eq 5) have been considered as alternate paths. From rough estimates, only one molecule fluoresces for 10^5 oxidized. Perhaps an unstable complex common to (1) and (5) is first formed between ${}^1O_2$ and R.

This reaction is an example of the light-emitting step proposed by Khan and Kasha[18] in their hypothesis about the role of ${}^1O_2$ in chemiluminescence.

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(12) In 1-chloronaphthalene both the rate of oxidation and *I* are lower than in *o*-$C_6H_4Cl_2$, but *I* is still three times larger than in C_6H_5I although chloronaphthalene is twice as viscous.

(13) *Cf.* C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(14) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

(15) In an Aminco spectrofluorimeter.

(16) Naphthacene, E_T = 29 kcal.

(17) See A. Yildiz, P. T. Kissinger, and C. N. Reilley, *J. Chem. Phys.*, **49**, 1403 (1968).

(18) A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, **88**, 1574 (1966).

The Cellulose Polymer Supported Sequential Analysis of Polyribonucleotides[1]

Sir:

Knowledge of the nucleotide sequence of polyribonucleotides of biological interest is a necessary prerequisite to understanding the process by which information coded in the nucleotide sequences of RNA molecules is translated into proteins. Any method for the sequential analysis of polyribonucleotides which proposes to be of practical value in gaining this knowledge must sequentially remove each nucleotide completely in a fast efficient step which can be repeated continuously without lengthy intermittent purifications. We wish to report such a procedure (Figure 1) accomplished by attaching polyribonucleotides to an insoluble cellulose support and sequentially removing the terminal base using an adaptation of the Whitfeld[2] periodate method.

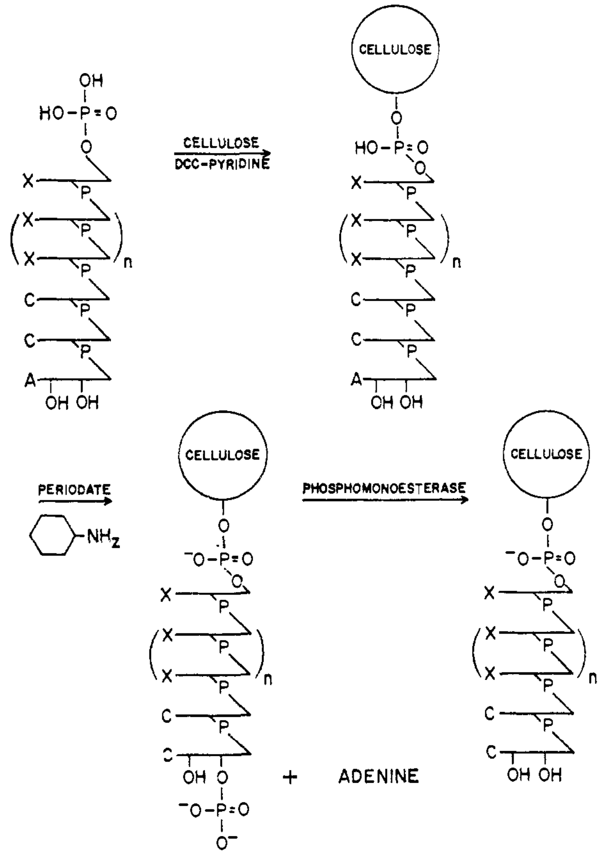

Figure 1. Schematic diagram of the attachment of sRNA to a cellulose support and subsequent removal of the 3′-terminal adenine base.

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(1) This research was supported by the Petroleum Research Fund, Grant 3190-B, administered by the American Chemical Society.

(2) P. R. Whitfeld, *Biochem. J.*, **58**, 390 (1959).