$$D_{CF_3O-OCF_3,298} = 360.2 \pm 3 - (319.6 \pm 3.5) = 40.6 \pm 5 \text{ kcal mol}^{-1}$$

This value may be compared to the corresponding values for dimethyl, diethyl, and di-*tert*-butyl peroxides, *i.e.*, 36.1 ± 1 ± 1, 34.1 ± 1, and 37.4 kcal mol^{-1}, respectively.[4] The bond in bistrifluoromethyl peroxide thus appears to be stronger than those in the dialkyl peroxides, although the difference is not outside of the error limits. A case for expecting a trend of this sort can be made using the arguments put forward to explain the high value for the oxygen–oxygen bond strength in dioxygen difluoride.[14–16] The answer to the question raised at the start of this article of the stability of CF_3OOCF_3 relative to dialkyl peroxides thus contains contributions from both factors mentioned there.

Although the study of a reaction equilibrium gives no direct information on the reaction paths involved, some comments can be made. The facts that[17] bistrifluoromethyl peroxide promotes the polymerization of hexafluoropropene at 275° and that the low molecular weight polymers had trifluoromethoxyl end groups constitute strong evidence that the initial step in the reaction involves cleavage of the oxygen–oxygen bond. In a recent study of the low-pressure pyrolysis of this compound,[18] carbon dioxide and carbonyl fluoride were observed as the main products, and the question as to whether the oxygen–oxygen bond of carbon–oxygen bond was the weaker was raised. In the present study, carbon dioxide is not a product and the equilibrium involves only the peroxide, trifluoromethyl hypofluorite, and carbonyl fluoride. These results are clearly most consistent with an oxygen–oxygen split. From a thermochemical point of view, it is possible to calculate the sum of the energy changes for the two-step process

$$CF_3OOCF_3 \longrightarrow CF_3OO + CF_3$$

$$CF_3OO \longrightarrow CF_3 + O_2$$

from the heats of formation of the peroxide and of the trifluoromethyl radical, which is −115.7 ± 2.0 kcal mol^{-1}.[5] This yields a value of 128.8 ± 4 kcal mol^{-1}. The allocation of the contributions of the individual carbon–oxygen bonds is not straightforward, but it may be pointed out that the corresponding values can be calculated from available thermodynamic data for hydrogen peroxide and estimated for dimethyl peroxide.[11] In each case, cleavage of the first bond to oxygen requires considerably more energy than does cleavage of the bond to oxygen in the R–OO radical. (The strength of the first carbon–oxygen bond in dimethyl peroxide is calculated as 71 kcal mol^{-1}, a value considerably below that usually cited[11] for the C–O bond dissociation energy, *i.e.*, 81.5 kcal mol^{-1}.) Cleavage of bistrifluoromethyl peroxide at the carbon–oxygen bond would be expected to require in excess of 65 kcal mol^{-1}, and on this basis the oxygen–oxygen cleavage is favored.

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(14) A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, *J. Amer. Chem. Soc.*, **81**, 6398 (1959).

(15) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

(16) R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **88**, 2394 (1966).

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(18) K. O. Christe and D. Pilipovich, *J. Amer. Chem. Soc.*, **93**, 51 (1971).

Iodine-Sensitized Photoformation of Singlet Oxygen

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Abstract: The use of iodine as a triplet sensitizer for production of singlet oxygen in hydrocarbon solution at room temperature has been investigated. The production of singlet oxygen was inferred from disappearance of an organic substrate, naphthacene or 1,3-diphenylisobenzofuran (DPIBF), upon irradiation. Direct excitation of I_2 molecules to the $^3\Pi_u$ state leads to the appearance of singlet oxygen, but the energy transfer reaction $^3I_2 + {}^3O_2 \rightarrow I_2 + {}^1O_2$ is some five orders of magnitude less efficient than the similar reaction involving naphthacene, $^3I_2 + \text{Nc} \rightarrow I_2 + {}^3\text{Nc}$. Other results of the studies are that naphthacene is two orders of magnitude less reactive with singlet oxygen than is DPIBF, and in the iodine–DPIBF system, all photooxidation is caused by iodine to oxygen direct energy transfer, whereas in the iodine–naphthacene system, nearly all singlet oxygen is generated by a two stage, iodine–naphthacene–oxygen energy transfer chain.

The detailed mechanisms of organic photooxidation processes have, in recent years, been the subject of several comprehensive investigations,[1,2] which have demonstrated that the triplet state of the absorbing organic species (sensitizer) is part of the energy transfer path and that this triplet state undergoes an energy transfer reaction with ground state oxygen molecules to produce excited singlet oxygen molecules which then add to the substrate to form the oxidation product(s). Although both autooxidations (sensitizer and oxidant identical) and sensitized oxidations (sensitizer and oxidant different) have been examined, in all cases reported to date the sensitizer has itself been an organic light absorber.

In principle, triplet state molecules other than those of an organic nature can also serve as sensitizers for

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(1) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

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

the production of singlet oxygen, provided only that they can be formed photochemically in relatively high yield and that their excitation energy exceeds that of the excited singlet oxygen $^1\Delta_g$ state. Among the simplest of such molecular triplet states are those of the halogen diatomic molecules, which because of heavy atom effects can readily be excited by direct photonic absorption. In the present study, the possibility of iodine serving as such a sensitizer has been examined, and it has been demonstrated that despite potentially complicating features such as iodine photodissociation and competing photochemical reactions, the only significant reaction occurring when iodine, oxygen, and a suitable organic photooxidant molecule in *n*-hexane are irradiated with light in the region of iodine singlet–triplet absorption is the photooxidation of the organic substrate.

Theory and Method

Two different organic molecules were chosen as oxidants in this work: 1,3-diphenylisobenzofuran (DPIBF) and naphthacene (tetracene). Both compounds fluoresce, both photooxidize readily and simply,[3,4] and both have absorption thresholds sufficiently high in energy to permit selective excitation of iodine in solutions containing both sensitizer and oxidant. They differ in one crucial respect: the energy of their lowest triplet state. The exact location of the DPIBF triplet is not known, but by comparison with analogous heterocyclic aromatics should be substantially higher in energy than the $^3\Pi_u$ state of iodine. For this system, therefore, the only energy transfer path available to form singlet oxygen is direct transfer ($^3I_2 + {}^3O_2 \rightarrow {}^1I_2 + {}^1O_2$). The naphthacene lowest triplet, on the other hand, is 10,250 cm^{-1} above the ground state,[4] placing it intermediate between the iodine triplet ($\sim$12,000 cm^{-1}) and oxygen singlet ($\sim$8000 cm^{-1}). For this system, therefore, an additional two-step energy transfer pathway is possible ($^3I_2 + \mathrm{Nc} \rightarrow I_2 + {}^3\mathrm{Nc}$; $^3\mathrm{Nc} + {}^3O_2 \rightarrow \mathrm{Nc} + {}^1O_2$). Furthermore, the transfer of energy from triplet naphthacene to singlet oxygen has been shown to be a relatively efficient process.[5]

Previous studies on the oxidants[3,4] have indicated that the production of singlet oxygen could be monitored by following the peroxidation reaction; for fluorescent compounds, this is conveniently accomplished by measuring the solution fluorescence as a function of time. In the presence of suitable filtering and upon verification by control experiments as described below, decay of solution fluorescence with time is due solely to photooxidation and can be related to singlet oxygen formation and reaction. The elementary reactions and kinetic expressions that lead from iodine excitation to photooxidation are detailed in the following paragraphs.

The photolysis of iodine itself in hydrocarbon solvents has been studied,[6] and it has been found that the $^3\Pi_u$ state of the molecule dissociates to give iodine atoms with a wavelength- and viscosity-dependent quantum yield ϕ_D of the order of 0.5. Since emission from iodine in solution is not observed, the following elementary reactions account for the fate of excited iodine molecules (an asterisk represents excess vibrational excitation energy).

$$^1I_2 + h\nu \longrightarrow {}^3I_2^* \qquad (1)$$

$$^3I_2^* \longrightarrow I + I \qquad (2)$$

$$^3I_2^* + M \longrightarrow {}^3I_2 + M \qquad (3)$$

$$^3I_2 \xrightarrow{k_4} {}^1I_2 \qquad (4)$$

$$^3I_2 + {}^3O_2 \xrightarrow{k_5} {}^1I_2 + {}^1O_2 \qquad (5)$$

If naphthacene is present in the system as well, additional energy transfer reactions must be considered (see below). For the moment, we restrict consideration to the DPIBF system.

The competition between reactions 2 and 3 yields the quantum yield for triplet iodine

$$\Phi(^3I_2) = 1 - \Phi_D \qquad (6)$$

Subsequently, the singlet oxygen yield can be expressed by

$$\Phi(^1O_2) = (1 - \Phi_D)k_5[O_2](k_4 + k_5[O_2])^{-1} \qquad (7)$$

In the presence of DPIBF (indicated by F in the following expressions), singlet oxygen will be consumed mainly through two reactions

$$^1O_2 \xrightarrow{k_8} {}^3O_2 \qquad (8)$$

$$^1O_2 + F \xrightarrow{k_9} FO_2 \qquad (9)$$

Whence the quantum yield for formation of peroxide (disappearance of F) is

$$\Phi(FO_2) = (1 - \Phi_D)\{k_5[O_2](k_4 + k_5[O_2])^{-1}\} \times \{k_9[F](k_8 + k_9[F])^{-1}\} \qquad (10)$$

In eq 10, the first term on the right is the triplet iodine yield, the second is the efficiency of energy transfer from iodine to oxygen, and the third is the efficiency of oxidation of F by singlet oxygen.

To find the rate of peroxide formation, conventional steady-state approximations can be utilized; alternatively, one need only multiply the quantum yield expression by the rate of photon absorption, which for sufficiently high sensitizer concentration and cell path length is essentially the rate of photon incidence I_0.

$$d(FO_2)/dt = I_0(1 - \Phi_D)k_5[O_2](k_4 + k_5[O_2])^{-1} \times k_9[F](k_8 + k_9[F])^{-1} \qquad (11)$$

Usually, one inverts the above expressions to obtain the equational basis for a Stern–Volmer treatment of kinetic data.[7]

$$d(FO_2)/dt^{-1} = I_0(1 - \Phi_D)^{-1} \times (1 + k_4/k_5[O_2])(1 + k_8/k_9[F]) \qquad (12)$$

Thus, for constant oxygen concentration, plots of the reciprocal rate *vs.* reciprocal concentration of F should be linear with a slope/intercept ratio of k_8/k_9. Values of the ratio k_4/k_5 can be obtained from similar plots involving oxygen concentration variations or can be found from quantum yield determinations using eq 10.

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(3) C. Dufraisse and S. Ecary, *C. R. Acad. Sci.*, **223**, 735 (1946).

(4) B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72**, 3468 (1968).

(5) B. Stevens and B. E. Algar, *Chem. Phys. Lett.*, **1**, 58 (1967).

(6) L. F. Meadows and R. M. Noyes, *J. Amer. Chem. Soc.*, **82**, 1872 (1960).

(7) O. Stern and M. Volmer, *Phys. Z.*, 20, 183 (1919).

Absolute knowledge of the rate constants such as k_5 is difficult to obtain and could be deduced from the above kinetic scheme only if the rate constant for the deactivation of triplet iodine to the ground state (k_4) were known. This rate constant has not, to our knowledge, been determined. However, additional data concerning k_5 emerge from analysis of the naphthacene photooxidation scheme.

To reactions 1–5 must be added two more involving energy transfer

$$^3I_2 + Nc \xrightarrow{k_{13}} {}^1I_2 + {}^3Nc \qquad (13)$$

$$^3Nc + {}^3O_2 \xrightarrow{k_{14}} Nc + {}^1O_2 \qquad (14)$$

Triplet naphthacene may be deactivated to the ground state

$$^3Nc \xrightarrow{k_{15}} Nc \qquad (15)$$

$$^3Nc + I_2 \xrightarrow{k_{16}} Nc + I_2 \qquad (16)$$

and the oxidation reaction now involves Nc rather than F

$$^1O_2 + Nc \xrightarrow{k_{9a}} NcO_2 \qquad (9a)$$

The expression for the quantum yield for peroxide formation is similar to eq 10 except for the middle term, which now represents a sum of two contributing pathways

$$\Phi(NcO_2) = (1 - \Phi_D)(k_4 + k_5[O_2] + k_{13}[Nc])^{-1} \times \{k_5[O_2] + k_{13}[Nc]k_{14}[O_2](k_{15} + k_{14}[O_2] + k_{16}[I_2])^{-1}\} \times k_{9a}[Nc](k_8 + k_{9a}[Nc])^{-1} \qquad (17)$$

As will be shown below, this rather formidable expression can be reduced to a more tractable form once values for some of the rate constant ratios are known.

Experimental Section

Materials. The solvent for these studies was *n*-hexane, purified by fractional distillation, after which fluorescence analysis showed no detectable impurities. Naphthacene (Eastman White Label) was purified by recrystallization from benzene followed by fractional sublimation under argon. The 1,3-diphenylisobenzofuran was synthesized in our laboratory following the procedure of Newman[8] and was purified by column chromatography followed by fractional sublimation under argon. Matheson AR grade iodine was used without further purification. Reinecke's salt for actinometry measurements was prepared from ammonium thiocyanate according to the procedure given by Wegner and Adamson.[9]

Instrumentation. Irradiations were carried out using a 900-W xenon arc lamp powered by a Christie regulated power supply (naphthacene irradiations) or a 75-W xenon lamp (DPIBF irradiations). In both cases, the lamp output was filtered through water-cooled Corning CS 3-68 and 3-69 filter combinations. The irradiation cells were 4-cm path length cylindrical Pyrex tubes with flat front and rear windows.

Actinometry measurements were made by irradiating solutions of Reinecke's salt in the same irradiation cells and with the same optical configuration as for the photochemistry runs, following the procedure and quantum yields given by Wegner and Anderson.[9]

Fluorescence spectra were measured on a Baird-Atomic Model SF-1 fluorescence spectrophotometer with a Hanovia 150-W xenon source and were recorded on a 10-in. strip chart recorder. For fluorescence measurements, portions of the irradiated solutions were transferred from the irradiation cell to 1-cm path length quartz cuvettes. Light source intensity fluctuations in the SF-1 were corrected for by comparing the sample fluorescence to that of a standard unirradiated solution of the oxidant.

Variations in oxygen concentration were achieved by bubbling a gas stream of appropriate composition (usually air or pure oxygen) through the sample after saturating the gas with *n*-hexane vapor to prevent solvent loss due to evaporation.

Absorption spectra, for actinometry and as a check on iodine concentration or charge-transfer complex formation, were recorded on a Perkin-Elmer Model 450 uv-visible recording spectrophotometer.

Concentrations. Except for solutions on which studies of iodine quenching behavior were carried out, all iodine-containing solutions had a concentration of 2.5×10^{-3} *M* iodine. Oxygen concentrations were computed from data of Berry and Burton[10] to be 2×10^{-3} *M* in air-saturated solution and 10^{-2} *M* in oxygen-saturated solution. Naphthacene and DPIBF concentrations utilized were in the range 5×10^{-6}–5×10^{-5} *M*. Stock solution concentrations were determined by weighing; concentrations of irradiated solutions were found by comparing the fluorescence intensity with that of an unirradiated standard solution.

Results

Control Experiments. To ascertain that the photochemical process under study was indeed photooxidation, uncomplicated by competing reactions, several irradiations were carried out with all but one of the necessary components present, using the same irradiation setup and for times in excess of those used under conditions where photooxidation occurred. The following solutions were so irradiated: (a) DPIBF, air-saturated (iodine absent); (b) DPIBF and iodine, argon-saturated (oxygen absent); (c) naphthacene, air-saturated (iodine absent); (d) naphthacene and iodine, argon-saturated (oxygen absent). In none of the above circumstances was any change of fluorescence intensity with irradiation time observed. Further, measurement of the iodine absorption spectra of irradiated solutions, including those undergoing photooxidation, revealed no evidence of iodine disappearance; the ultimate result of iodine dissociation in these solutions is apparently atom–atom recombination. From the above, it is clear that the presence of iodine as a sensitizer is necessary, with the filters used in this work, if reaction is to occur and that oxygen must be present also before any photochemistry takes place. We conclude that the reaction under observation is the clean photooxidation of the oxidant.

To verify that the fluorescence analysis and actinometric techniques used in this work gave results consistent with those determined by other means, the autooxidation of naphthacene was studied. For this process, Stevens and Algar[5] have shown that the quantum yield can be expressed by the relation

$$\Phi(NcO_2) = \gamma_{ISC}k_{14}[O_2](k_{14}[O_2] + k_{15})^{-1} \times k_{9a}[Nc](k_{9a}[Nc] + k_8)^{-1} \qquad (18)$$

Using $\gamma_{ISC} = 0.63$, $k_{15}/k_{14} = 1.8 \times 10^{-6}$, and $k_8/k_{9a} = 1.7 \times 10^{-3}$ determined by Stevens and Algar, the initial quantum yield for auto- and photooxidation of naphthacene in a 5×10^{-6} *M* solution is calculated to be 1.8×10^{-3}, independent of oxygen concentration above 10^{-3} *M*. Experimentally, we find for such a solution, either air- or oxygen-saturated, an initial quantum yield of 1.3×10^{-3}. The two values agree to within their respective uncertainties.

Absence of charge-transfer complex formation in solutions of naphthacene–iodine and DPIBF–iodine

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[8] M. S. Newman, *J. Org. Chem.*, **26**, 2631 (1961).

[9] E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 396 (1966).

[10] P. J. Berry and M. Burton, *J. Chem. Phys.*, **23**, 1969 (1955).

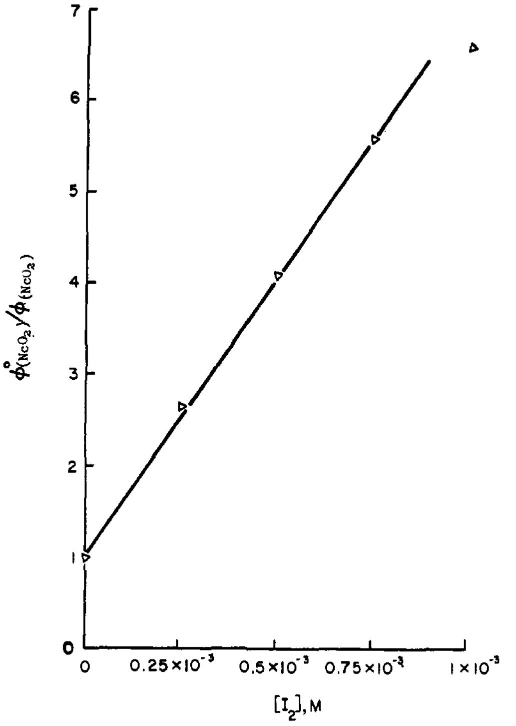

Figure 1. Variation of initial quantum yield of naphthacene autooxidation with iodine concentration.

was verified by measuring the absorption spectra of solutions of the individual compounds and comparing with the absorption spectra of the mixture. Strict additivity was observed, whereas for systems where charge-transfer complexes are known to occur (*e.g.*, 2.5-dimethylfuran), nonadditivity was obvious.

Iodine Quenching. The presence of the quenching reaction $^3Nc + I_2 \rightarrow Nc + I_2$ in the kinetic scheme for photosensitized oxidation of naphthacene requires that knowledge be obtained about the rate constant for this process. This was done by comparing the initial rate for naphthacene autooxidation in the presence and absence of iodine, under illumination conditions such that only naphthacene was absorbing radiation. Under these circumstances, one must add to the kinetic scheme for autooxidation the quenching reaction (reaction 16) for triplet naphthacene and also quenching reactions, leading possibly to triplet naphthacene or to ground state naphthacene, for singlet naphthacene. One then obtains for the quantum yield ratio

$$\Phi_0(NcO_2)/\Phi(NcO_2) = (\gamma_{ISC}/\gamma'_{ISC}) \times \{1 + k_{16}[I_2](k_{14}[O_2] + k_{15})^{-1}\} \quad (19)$$

In this expression, γ'_{ISC}, the yield of triplet naphthacene in the presence of iodine, depends on iodine concentration and also on the partitioning of quenching products between ground state and triplet state naphthacene. The latter is unknown, but one can set limits on it by noting that fluorescence quenching of naphthacene by iodine only amounts to about 30% at the highest concentration of iodine used in this facet of the work. If this quenching results solely in ground state naphthacene, $\gamma'_{ISC} = (0.70)(0.63) = 0.44$. If it results solely in triplet naphthacene, $\gamma'_{ISC} = 0.44 + 0.30 = 0.74$. Thus, the ratio in eq 19 is between 0.63/0.44 and 0.63/0.74, or 1.15 ± 0.30.

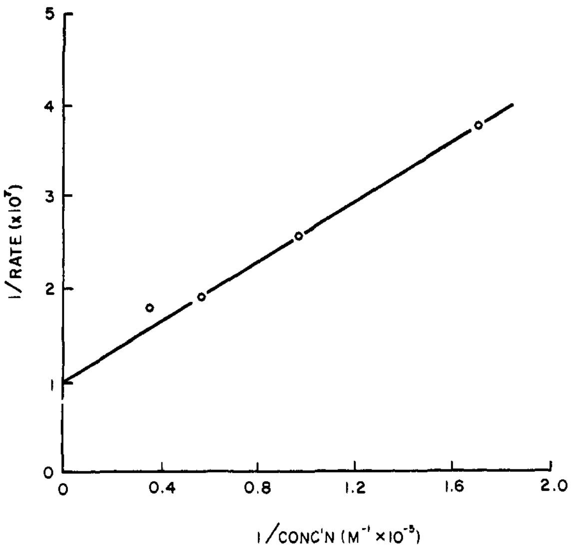

Figure 2. Iodine-sensitized photooxidation of 1,3-diphenylisobenzofuran. Plot of reciprocal reaction rate *vs.* reciprocal concentration.

A plot of the experimental results for $\Phi_0(NcO_2)/\Phi(NcO_2)$ at various iodine concentrations is shown in Figure 1. It can be seen to be reasonably linear, verifying that the variation in γ'_{ISC} with iodine concentration is small relative to the other effects. From its slope, recalling that $[O_2] = 2 \times 10^{-3}$ *M* and $k_{15} \ll k_{14} \cdot [O_2]$, we obtain $k_{16}/k_{14} = 11 \pm 3$ (the deviation of the experimental values from linearity at the upper limit of iodine concentration used is most likely due to sensitized oxidation occurring at this higher concentration, since iodine absorption may no longer be negligible even with efficient filtering of the exciting light).

Sensitized Oxidation of DPIBF. The results of the iodine-sensitized photooxidation of 1,3-diphenylisobenzofuran were interpreted using eq 12. As it predicts, the variation of concentration of DPIBF with irradiation time was nonlinear; this variation (in the form of fluorescence intensity of the sample) was plotted and the slope of the concentration–time curve, which is proportional to the rate of oxidation, was determined for several different concentrations. When the reciprocal rate so determined was plotted against reciprocal concentration, a linear plot was obtained (Figure 2), whose slope–intercept ratio gave $k_8/k_9 = 1.5 \times 10^{-5}$ $l.^{-1}$ mol.

Because it was difficult to control oxygen concentration sufficiently to determine Stern–Volmer plots for that concentration variable, information about the iodine–oxygen energy transfer was obtained by measurement of the initial quantum yield for photooxidation of air-saturated solutions with application of eq 10. The iodine dissociation quantum yield was estimated by convoluting the transmission curve of the filter combination with manufacturer's data on the spectral output of the xenon lamp to obtain the most probable wavelength of light absorbed (the sample absorbed essentially all light throughout the filter transmission region), for which wavelength the dissociation quantum yield was interpolated from data of Meadows and Noyes[6] to be 0.4.

The initial quantum yield for a 4.0×10^{-5} *M* DPIBF solution, determined from fluorescence decrease together with Reinecke's salt actinometry, was found to be $\Phi(FO_2)_0 = 7 \times 10^{-4}$. Inserting this value into eq 10 along with the above-determined value of k_8/k_9 yielded the result $k_4/k_5 = 1.25$ l.$^{-1}$ mol.

Sensitized Oxidation of Naphthacene. The experimental results for the iodine-sensitized disappearance of naphthacene as determined by decay of fluorescence are shown in Figure 3. In distinction to the DPIBF results, in this case first-order kinetics were observed, for both air-saturated and oxygen-saturated solutions, despite the complex concentration dependence predicted by eq 17. However, if experimental values for various rate constant ratios are utilized, eq 17 can be reduced to quasi-first-order form.

The value of k_8/k_{9a} is 1.7×10^{-3} l.$^{-1}$ mol, determined by Stevens and Algar.[4] Since the naphthacene concentrations in these experiments was $\leqq 5 \times 10^{-6}$ *M*, this establishes the inequality $k_8 > 100k_{9a}[Nc]$, from which the last term in eq 17 becomes $k_{9a}[Nc]/k_8$. As determined above, $k_{16}/k_{14} = 11$; again, from Stevens and Algar, $k_{15}/k_{14} = 1.8 \times 10^{-6}$; whence, since iodine and oxygen concentrations were approximately the same in these solutions, $k_{15} + k_{14}[O_2] + k_{16}[I_2] \sim k_{16} \cdot [I_2]$. Noting also that $k_4 \gg k_5[O_2]$ as determined above, the simplified form of eq 17 is

$$\Phi(NcO_2) = (1 - \Phi_D)(k_{9a}/k_8)[Nc] \times (0.09 + k_5[O_2]/k_{13}[Nc])(1 + k_4/k_{13}[Nc])^{-1} \quad (20)$$

Thus, if either $0.09k_{13}[Nc] \gg k_5[O_2]$, k_4 or $k_5[O_2]$, $k_4 \gg k_{13}[Nc]$, first-order kinetics result, and even for intermediate values, the variation in the quotient term is small compared to the variation in [Nc].

The values obtained for initial quantum yields at different naphthacene and oxygen concentrations are summarized in Table I, which also gives the value of k_5/k_{13} calculated from these results using eq 20.

Table I. Results of Sensitized Photooxidation of Naphthacene

[Nc]	$[O_2]$	$\Phi_i(NcO_2)$	k_5/k_{13}
5.7×10^{-6}	2×10^{-3}	2.9×10^{-5}	1.4×10^{-5}
5.7×10^{-6}	1×10^{-2}	1.2×10^{-4}	1.0×10^{-5}
2.8×10^{-6}	2×10^{-3}	1.1×10^{-5}	1.0×10^{-5}
2.8×10^{-6}	1×10^{-2}	5.7×10^{-5}	1.9×10^{-5}

Discussion

Rate constant ratios as determined in this study for processes occurring in hexane solution are summarized in Table II. From these values, several conclusions can be drawn regarding compounds used in this study.

Table II. Rate Constant Ratios for Iodine-Sensitized Photooxidation of Naphthacene and 1,3-Diphenylisobenzofuran

Ratio	Value	Source
k_8/k_9	1.5×10^{-5} l.$^{-1}$ mol	Sens ox. DPIBF
k_4/k_5	1.25 l.$^{-1}$ mol	Sens ox. DPIBF
k_{15}/k_{14}	1.8×10^{-6} l.$^{-1}$ mol	Ref 4
k_5/k_{13}	1.4×10^{-5}	Sens ox. Nc
k_{16}/k_{14}	11	Iodine quenching
k_{9a}/k_9	10^{-2}	Sens ox. DPIBF

Diphenylisobenzofuran is seen to react with singlet oxygen about 100 times faster than does naphthacene, a result which is consistent with Wilson's observation[11] that DPIBF is 20 times as reactive as rubrene (tetramethylnaphthacene). Combining these results gives a reactivity for rubrene that is five times that of naphthacene. Thus, it appears that for naphthacene, as for anthracene (Bowen and Tanner[12] and Livingston and Rao[13] both found faster oxidation rates for 9,10-diphenylanthracene than for anthracene), substitution at the positions where oxygen adds enhances the reactivity. Such substitution apparently lowers the activation energy for the bridging of the aromatic ring by singlet oxygen.

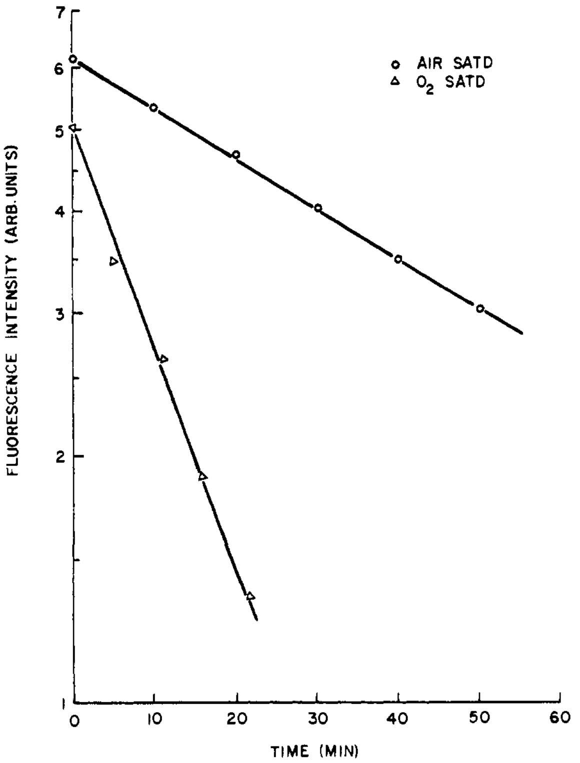

Figure 3. Iodine-sensitized photooxidation of naphthacene. Semilogarithmic plot of fluorescence intensity *vs.* irradiation time (initial naphthacene concentration 5×10^{-6} *M*).

The energy transfer path, $^3I_2 \rightarrow {}^1O_2$, has been demonstrated to exist in hydrocarbon solution. However, it has also been shown that the transfer step $^3I_2 \rightarrow {}^1O_2$ is some five orders of magnitude less efficient than the $^3I_2 \rightarrow {}^3Nc$ transfer step. This reduced efficiency might be caused by efficient quenching of the triplet state of iodine by oxygen, resulting in ground state products rather than in singlet oxygen.

$$^3I_2 + {}^3O_2 \longrightarrow I_2 + {}^3O_2 \quad (21)$$

Our experiments do not entirely rule out this possibility, but they do provide strong evidence against it, derived from the results of the sensitized oxidation of naphthacene. The kinetic scheme including reaction 21 is quite complex, but it can be simplified for the extreme cases when reaction 21 is negligible and when it is predominant over reactions 4 and 5. Using the kinetic scheme neglecting reaction 21, the values reported in Table I are obtained for the ratio k_5/k_{13} at different initial concentrations of naphthacene and oxygen. These are consistent with one another within

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(11) T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

(12) E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955).

(13) R. Livingston and V. S. Rao, *J. Phys. Chem.*, **63**, 794 (1959).

about 30%. Using the kinetic scheme that assumes reaction 21 to be predominant, on the other hand, the different initial concentrations give k_5/k_{13} ratios that differ from each other by two orders of magnitude (but are still in the range 10^{-4}–10^{-6}). In other words, the variation of initial quantum yields with reactant concentrations seems to be incompatible with the reaction scheme in which reaction 21 is predominant.

It thus appears that, in contrast to systems in which oxygen interacts with polyatomic organic triplet state molecules, the oxygen–iodine triplet state interaction yields a slow rate of triplet quenching and energy transfer. Two possible causes of this slow rate can be put forward, one of them due to the diatomicity of the triplet molecules, the other due to the presence of heavy atoms.

In the first instance, one notes that there is an exothermicity of the energy transfer reaction of some 4000 cm^{-1} that must be absorbed either by the single vibrational mode of the diatomic molecules or by the solvent "sink." This represents a quite severe restriction compared to energy transfer from I_2 to naphthacene or from naphthacene to O_2, where the participation of a polyatomic molecule in the reaction provides multiple channels, in the form of a large number of vibrational modes, to accept the excess energy. Put in other words, the energy density of final states is enormously higher for the energy transfer reaction involving one polyatomic participant than for one involving two diatomic participants.

Alternatively, one could view the I_2–O_2 interaction as involving complex formation

$$^{3}I_2 + {}^{3}O_2 \rightleftarrows {}^{5}(I_2\cdot O_2) \qquad (22a)$$

$$\rightleftarrows {}^{3}(I_2\cdot O_2) \longrightarrow I_2 + {}^{3}O_2 \qquad (22b)$$

$$\longrightarrow {}^{1}(I_2\cdot O_2) \longrightarrow I_2 + {}^{1}O_2 \qquad (22c)$$

with the singlet, triplet, and quintet states of the complex all being excited electronic states. In this case, the intersystem crossing reaction

$$^{1}(I_2\cdot O_2) \longrightarrow {}^{3}(I_2\cdot O_2) \qquad (23)$$

would be heavy-atom enhanced to a great degree and, being an intersystem crossing from excited singlet to triplet, could be extremely rapid provided that the tetratomic complex could be likened to a polyatomic system where such intersystem crossing competes favorably with fluorescence. The low rate of singlet oxygen formation would then be due to the competitiveness of reaction 23 with 22c. Whether or not excimer complexes between iodine and oxygen exist is an open question. We have observed apparent inhibition of oxygen-induced fluorescence quenching when iodine is added to a fluorescent solution, which may be taken as evidence for iodine–oxygen complex formation and thus lends some support to the complexation hypothesis. The evidence, however, is not at all conclusive.

In the iodine-sensitized photooxidation of naphthacene, as a result of the large differences between energy transfer efficiencies, virtually all of the photooxidation is effected by iodine–naphthacene–oxygen energy transfer. In the iodine-sensitized photooxidation of 1,3-diphenylisobenzofuran, on the other hand, the only energetically allowed transfer path is the direct iodine–oxygen transfer step. For this system, despite the high efficiency of the DPIBF oxidation step, low quantum yields have been found because of the low efficiency of the energy transfer process.

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Quenching of Photophysically Formed Singlet ($^1\Delta_g$) Oxygen in Solution by Amines[1]

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Abstract: The quenching by amines of singlet ($^1\Delta_g$) oxygen formed in Freon-113 solution by laser excitation within the $^1\Delta_g + 1v \leftarrow {}^3\Sigma_g^-$ oxygen absorption band envelope has been studied by inhibition of the oxidation of tetraphenylcyclopentadienone (tetracyclone). The quenching rate constants range from 3.1×10^4 l. mol^{-1} sec^{-1} for ethylamine to 2.1×10^6 l. mol^{-1} sec^{-1} for triethylamine and correlate with the ionization potential of the quencher.

If a solution of oxygen in Freon-113 is irradiated in the $^1\Delta_g + 1v \leftarrow {}^3\Sigma_g^-$ absorption band envelope with the 1.065-μm output from a Nd-YAG laser, singlet oxygen ($^1\Delta_g$) is produced unambiguously and in quantity.[2] Other techniques for producing singlet oxygen are low-pressure microwave discharge in the gas phase and in solution by chemical means or dye photosensitization.[3] It is possible that in these other techniques extraneous chemical species may be produced and cause reactions which could be mistaken for those of singlet oxygen.

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(1) Presented at the 6th International Conference on Photochemistry, 1971.

(2) I. B. C. Matheson and John Lee, *Chem. Phys. Lett.*, 7, 475 (1970).

(3) For recent years' reviews of the generation and properties of singlet oxygen, see *Ann. N. Y. Acad. Sci.*, **171**, 1 (1970).