J. Am. Chem. Soc. **1980**, *102*, 5656-5661

phenylphosphine oxide. The resulting oil was rechromatographed on a thick layer plate to give 300 mg (73%) of a pale yellow oil which was identical in all respects with a sample of methyl 4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (**33**) isolated from the photolysis of cyclopropene **29**.

Triplet-Sensitized Irradiation of Methyl 4-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butenoate (29). A solution containing 200 mg of **29** and 100 mg of thioxanthen-9-one in 500 mL of benzene was irradiated for 2.5 h under an argon atmosphere, using a 450-W Hanovia lamp equipped with a uranium glass filter sleeve. The solution was concentrated under reduced pressure and the resulting residue was chromatographed on a thick layer plate, using a 9% ether–hexane mixture as the eluent. The major component from the reaction mixture contained 150 mg (75%) of a crystalline solid, mp 67–68 °C, whose structure was assigned as *exo*-6-carbomethoxy-3-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**34**) on the basis of its spectral properties: IR (KBr) 3.40, 5.81, 6.50, 6.71, 6.90, 7.03, 7.32, 7.56, 8.31, 8.50, 8.62, 13.48, 13.83, 14.26, and 14.44 μm; NMR ($CDCl_3$, 100 MHz) δ 1.35 (s, 3 H), 2.20 (d, 1 H, J = 9.0 Hz), 2.76 (dd, 1 H, J = 9.0 and 5.0 Hz), 3.05 (d, 1 H, J = 5.0 Hz), 3.52 (s, 1 H), 3.66 (s, 3 H), and 7.0–7.6 (m, 10 H); UV (95% ethanol) 238 nm (ε 13 000); m/e 304 (M^+), 289, 245, 205, and 77.

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.65; H, 6.70.

Quantum-Yield Determinations. All quantitative measurements were made on a rotating assembly at room temperature, using a Rayonet reactor equipped with 3000-Å lamps. Samples were degassed to 5×10^{-3} mm in three freeze-thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum-yield determinations.[61] Reliably reproducible output rates of 1.73×10^{17} quanta/s were recorded. After the irradiation the degree of reaction was determined by quantitative LC analysis. An Altex 3.2 × 250 mm Lichrosorb 5-m C-18 reverse phase column with aqueous methanol was used for the analyses. The conversions were run to 15% or less. The mass balances in these runs were generally better than 95%.

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Charge-Transfer Mechanism for Quenching of the Lowest ^{3}n,π* State of Vapor-Phase Carbonyl-Containing Compounds by O_2

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Abstract: Rate constants, ranging between 0.20 and 6.9×10^9 M^{-1} s^{-1}, for quenching of the lowest ^{3}n,π* state of several carbonyl-containing compounds by oxygen in the vapor phase have been measured with a flash sensitization technique. In general, the rate constants increase with increasing energy of the ^{3}n,π* state, have small negative activation energies, and increase as the difference in energy between the ionization potential and triplet state energy of the carbonyl-containing compounds decreases. This is in accordance with coupling of the initially formed complex to a charge-transfer state. Spectroscopic evidence was obtained for the existence of a complex between acetone and oxygen.

Introduction

Oxygen has two excited electronic singlet states at energies less than the triplet-state energy of most organic molecules,[1] which allows oxygen to quench these triplet states by both intermolecular transfer of electronic energy and enhancement of intersystem crossing. Both processes are expected to occur through the formation of a complex with allowed singlet, triplet, or quintet spin multiplicity. However, spin selection rules allow the transfer of energy to occur only through the singlet-state complex and disallow relaxation of the quintet-state complex. Hence processes 1 and 2 are expected to be most important.

$$\mathrm{T} + \mathrm{O_2} \underset{k_{-c}}{\overset{1/9k_c}{\rightleftarrows}} {}^1(\mathrm{T}\cdots\mathrm{O_2})^* \xrightarrow{k_{et}} \mathrm{S_0} + \mathrm{O_2}^* \qquad (1)$$

$$\mathrm{T} + \mathrm{O_2} \underset{k_{-c}}{\overset{1/3k_c}{\rightleftarrows}} {}^3(\mathrm{T}\cdots\mathrm{O_2})^* \xrightarrow{k_{isc}} \mathrm{S_0} + \mathrm{O_2} \qquad (2)$$

$$\mathrm{T} + \mathrm{O_2} \underset{k_{-c}}{\overset{5/9k_c}{\rightleftarrows}} {}^5(\mathrm{T}\cdots\mathrm{O_2})^* \qquad (3)$$

T and S_0 are the triplet state and ground state of the organic molecule, respectively. The collision partners in reactions 1, 2, and 3 collide with rates given by $^1/_9k_c$, $^1/_3k_c$, and $^5/_9k_c$, respectively, where k_c is the hard sphere collisional rate constant and $^1/_9$, $^1/_3$, and $^5/_9$ are the statistical probabilities for formation of a complex with singlet, triplet, and quintet spin multiplicity, respectively. The collision complex dissociates with a rate constant k_{-c} to form reactants.

Extensive studies of the quenching of triplet-state aromatic hydrocarbons by oxygen in dilute solution have yielded quenching constants, k_q, which are less than $^1/_9k_d$ (where k_d is the rate constant for diffusional contact), indicating the predominance of process 1.[2,3] Exceptions, for which k_q approaches $^1/_3k_d$, include several stilbene derivatives for which it has been suggested that the small energy difference between the lowest excited singlet and triplet states in "twisted" geometries facilitates quenching through the formation of triplet-state complexes (process 2).[4] In ref 2 and 3 it was found that k_q decreases with increasing triplet energy of the aromatic. This was attributed to control of quenching by Franck–Condon factors associated with C–H stretching modes, and Siebrand's expressions for radiationless decay rates[5] were used to explain the results.[6]

The mechanism for quenching of ^{3}n,π* states seems to be less well understood. Merkel and Kearns have reported that the

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[1] G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, Princeton, N.J., 1950.

[2] L. K. Patterson, G. Porter, and M. Topp, *Chem. Phys. Lett.*, 7, 612 (1970).

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[4] J. L. Saltiel and B. Thomas, *Chem. Phys. Lett.*, **37**, 147 (1976).

[5] W. Siebrand, *J. Chem. Phys.*, **46**, 440 (1967); **47**, 2411 (1967).

[6] O. L. J. Gijzeman and F. Kaufman, *J. Chem. Soc., Faraday Trans. 2*, **69**, 72 (1973).

0002-7863/80/1502-5656$01.00/0

quenching constants of several triplet state aromatic ketones in carbon tetrachloride range between 1.1×10^9 and 3.8×10^9 M^{-1} s^{-1}, corresponding to $k_d/30$ to $k_d/10$, and show little dependence on molecular size and triplet energy.[7] The authors speculated that the small magnitude of these quenching constants relative to those for aromatics is due to the lesser accessibility of n orbitals for interaction with molecular oxygen. They also noted that k_q decreases as the energy gap between ^{3}n,π* and ^{3}π,π* states of these compounds decreases.

In contrast, Garner and Wilkinson have found that oxygen quenching constants are larger for some triplet state aromatic amines and ketones in benzene solution (range $1.4-14.0 \times 10^9$ M^{-1} s^{-1}) than for the aromatic hydrocarbons in ref 2 and 3.[8] Furthermore, their quenching constants do not decrease with increasing triplet energy but instead show a rough trend, with several exceptions, of increasing with increasing triplet-state energy. These authors attributed the higher rate constants to efficient coupling of the excited-state complex to low-lying triplet charge-transfer states, but they presented no direct experimental evidence for such complexes.

The results of ref 1, 2, 7, and 8 reveal different quenching behaviors for ^{3}n,π* and ^{3}π,π* states. However, it is difficult to compare the two since the differences between the results reported in ref 7 and 8 make it difficult to establish the mechanism for quenching of ^{3}n,π* states by oxygen. These differences may arise from the lack of pure ^{3}n,π* state character, which results from the mixing of ^{3}n,π* and ^{3}π,π* states. Furthermore, the different solvent cage effects in ref 7 and 8 may affect the rate constants differently.

In order to overcome these solvent effects we have measured the quenching constants of several triplet-state aldehyde and ketone vapors in an attempt to determine the mechanism for quenching of ^{3}n,π* states.

Experimental Section

Chemicals. Chromatoquality benzene with a stated purity of 99.9% was obtained from Matheson Chemical Co. The aldehydes and ketones were of the highest purity available from Aldrich Chemical Co., Tridom Chemical, Inc., and Matheson Chemical Co. Research-grade oxygen was obtained from Air Products Co.

Benzil was recrystallized six times from absolute ethanol and washed with hexane, and benzaldehyde was distilled twice under vacuum. All other chemicals were used without further purification. This procedure was found to be adquate since, where comparison was possible (for all compounds except 1-indanone, benzil, and 1-phenyl-1,2-propanedione), unquenched triplet-state lifetimes agreed well with literature values. Furthermore, the rate constants for quenching of undistilled and twice-distilled benzaldehyde were the same, and several of our quenching constants in Table I agree with previously reported values. All samples were deoxygenated by three or four freeze-pump-thaw cycles before study.

All room-temperature experiments were done at 25 ± 2 °C.

Fixed pressures of benzene within the range 2-10 Torr were used in each gas mixture. The pressures of 1-indanone, benzophenone, benzil, and 1-phenyl-1,2-propanedione were established by their room-temperature vapor pressures. Pressures of the other carbonyl-containing compounds were less than 0.10 Torr except the acetone pressure, which was 0.50 Torr. The oxygen pressures ranged between 5 and 120 mTorr.

Equipment. The flash excitation and detection equipment used in the lifetime experiments was the same as that described previously with the exception that different Corning Glass Co. cutoff filters, which transmit mostly wavelengths longer than the 0,0 wavelength of phosphorescence, were placed over the photomultiplier.[9]

Absorption spectra were recorded with a Cary 14 UV-visible spectrophotometer of mixtures in a 10-cm cell containing 40 Torr acetone in the absence and presence of 350 Torr oxygen. The reference cell contained 350 Torr oxygen for both spectra.

Method. Triplet-state aldehyde and ketone molecules were collisionally sensitized by triplet-state benzene molecules which were formed by flash excitation. This method has several advantages over direct excitation of the carbonyl-containing molecule. First, the extinction coefficient for $S_0 \rightarrow S_1$ absorption by some of the aldehydes and ketones is small and necessitates the use of relatively high pressures of these compounds, which, in some cases, may only be achieved by heating the sample. However, the lifetime and efficiency for quenching of the triplet state of some carbonyl-containing compounds are sensitive to temperature, and comparison of quenching constants of different compounds at different temperatures would be misleading. Triplet-state sensitization by benzene overcomes this problem because benzene has a high vapor pressure, a relatively large extinction coefficient for $S_0 \rightarrow S_1$ absorption, a large $S_1 \rightarrow T_1$ intersystem crossing quantum yield, and a triplet state which is sufficiently long lived to allow adequate sensitization of carbonyl triplets at room-temperature vapor pressures. Second, the chances of impurity quenching are reduced at lower pressures of carbonyl-containing compounds. Third, self-quenching of phosphorescence by ground-state molecules, observed for some carbonyl-containing compounds,[10,11] is minimized.

Two possible problems of this sensitization method are formation of emissive complexes between triplet-state benzene and the aldehyde or ketone and reaction between triplet-state benzene and the aldehyde or ketone. However, these appeared to be negligible at the pressures used since, where comparison is possible, the phosphorescence lifetimes were the same for benzene-sensitized and directly sensitized (through $S_0 \rightarrow S_1$ absorption) phosphorescence of the carbonyl-containing compounds, and the lifetimes and intensity of phosphorescence did not change after repeated flashes of the excitation source.

The complete mechanism for sensitization is believed to be similar to that presented in ref 9 but need not be known completely in order to interpret the results. Moreover, the low pressures of the aldehydes and ketones ensure that little singlet-singlet energy transfer occurs, and thus only triplet-state processes need to be considered.[12]

In all experiments the phosphorescence reached maximum intensity at time t_{max} in less than 10-100 μs and decayed exponentially over a much longer time scale. This is consistent with the following mechanism.

$$^3B \rightarrow B \tag{4}$$

$$^3B + B \rightarrow 2B \tag{5}$$

$$^3B + O_2 \rightarrow B + O_2^* \tag{6}$$

$$^3B + C \rightarrow B + {}^3C \tag{7}$$

$$^3C \rightarrow C + h\nu \tag{8}$$

$$^3C \rightarrow C \tag{9}$$

$$^3C + C \rightarrow 2C \tag{10}$$

$$^3C + O_2 \xrightarrow{k_q} C + O_2^* \tag{11}$$

$$^3C + B \rightarrow \text{products (negligible)} \tag{12}$$

B and C refer to benzene and the carbonyl-containing compounds, respectively. It is assumed that the benzene pressure is sufficiently high and the lifetime of ^{3}C is long enough to guarantee that processes 4-12 occur from vibrationally relaxed excited states.

Expression 13, which relates the phosphorescence lifetimes in the absence, τ_p^0, and presence, τ_p, of molecular oxygen, is consistent with this mechanism.

$$\tau_p^{-1} = \tau_p^{0^{-1}} + k_q(O_2) \tag{13}$$

The reciprocal lifetime was determined from the slope of a linear plot of ln I_p vs. time, where I_p is the intensity of phosphorescence at times well after t_{max}, and k_q was determined from the slope of a plot of τ_p^{-1} vs. (O_2).

Results

Typical plots of τ_p^{-1} vs. (O_2) and the quenching constants appear in Figure 1 and Table I, respectively. Also included in Table I are quenching constants reported in the literature.

Figure 2 shows typical Arrhenius plots for the quenching constants, and the corresponding activation energies and antiln of intercepts are in Table II.

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(7) P. B. Merkel and D. R. Kearns, *J. Chem. Phys.*, **58**, 398 (1973).

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(11) M. Berger, I. L. Goldblatt, and C. Steel, *J. Am. Chem. Soc.*, **95**, 1717 (1973).

(12) In the case of acetone sensitization some singlet-singlet energy transfer does occur at the relatively high acetone pressure. However, this process and the fate of the excited singlet state acetone molecules apparently have little effect on our results since values for the lifetime of and rate constant for quenching by oxygen of the acetone triplet state agree well with literature values.

Table I

compd	$k_q \times 10^{-9}$, M^{-1} s^{-1}	ref	E_{T_1}, cm^{-1}	ionization potential, eV	ref
benzil (1)	0.20 ± 0.01	this work	18 800	9.1	27
1-phenyl-2,3-diketopropane	0.28 ± 0.02	this work	~19 000		
trans-glyoxal (2)	0.056	28	19 198	10.6	29
biacetyl (3)	0.51 ± 0.04	this work	20 000	9.25	30
	0.52 ± 0.04	31			
2,3-pentanedione	0.56 ± 0.04	this work	~20 000		
benzophenone (4)	0.99 ± 0.07	this work	24 650	9.45	32
benzaldehyde (5)	2.1 ± 0.15	this work	25 130	9.51	30
	2.9	11			
acetophenone (6)	4.7 ± 0.3	this work	25 800	9.65	32
hexafluoroacetone (7)	0.45	33	26 250	11.68	34
1-indanone	4.9 ± 0.3	this work	26 546		
acetone (8)	6.9 ± 0.5	this work	28 200	9.69	30
	8.2	20			
acetone-d_6	6.9 ± 0.5	this work	~28 000		
acetaldehyde (9)	5.4 ± 0.4	this work	~29 300	10.21	30

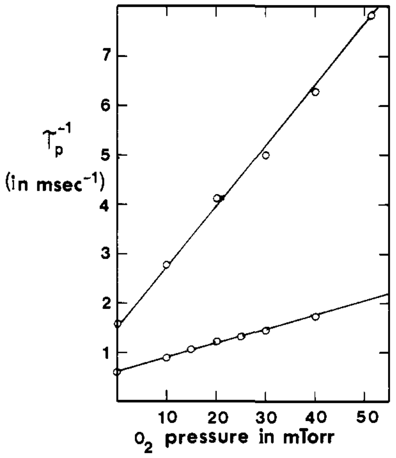

Figure 1. The top curve and bottom curve are plots of τ_P^{-1} vs. O_2 pressure for benzaldehyde and biacetyl, respectively. The benzaldehyde and biacetyl pressures were 100 and 20 mtorr, respectively.

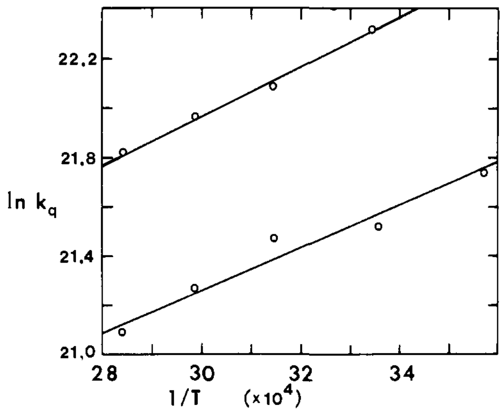

Figure 2. Arrhenius plots for acetophenone (top curve) and benzaldehyde (bottom curve).

Table II. Arrhenius Plots of Quenching Constants

compd	energy, cm^{-1}	activation energy, kcal/mol	antiln of intercept × 10^{-8}, s^{-1} [a]
biacetyl	20 000	−1.6 ± 0.2	0.41
benzaldehyde	25 130	−1.7 ± 0.2	1.4
acetophenone	25 800	−2.0 ± 0.3	1.6
acetone	28 200	−1.7 ± 0.2	4.3

[a] These numbers correspond to $k_{et}/9 + k_{isc}/3$ for molecules in set 1 (see eq 16 and Discussion section). However, the numbers are relative values dependent upon the units used for k_q.

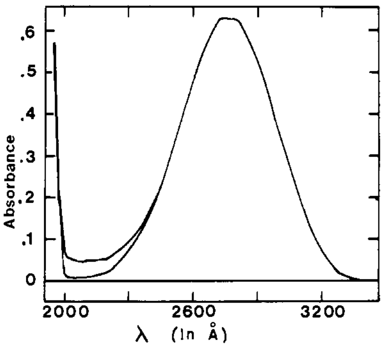

Figure 3. The bottom curve is the absorption spectrum for 40 torr acetone. The top curve is the absorption spectrum for a mixture containing 40 torr acetone plus 350 torr oxygen. The difference spectrum (not shown) is that of a ground-state acetone–oxygen complex.

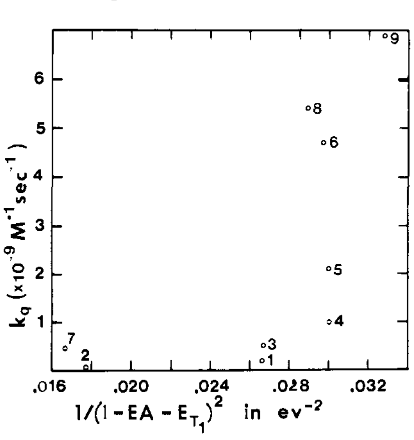

Figure 4. Plot of k_q vs. $1/(I - EA - E_{T_1})^2$ in eV^{-2}. The numbers beside the points identify the compounds according to Table I.

Figure 3 shows the absorption spectra for 40 Torr of acetone in the absence and presence of 350 Torr of oxygen.

Figure 4 is a plot of k_q vs. $1/(I - EA - E_{T_1})^2$ for the designated rate constants in Table I. The ionization potentials of the carbonyl compounds, I, electron affinity of oxygen, EA, and lowest triplet state energies of the carbonyl compounds, E_{T_1}, were obtained from the literature.

Discussion

Before the quenching mechanism is discussed, the nature of the electronic state being quenched should be considered. The lowest triplet state of all compounds in Table I is believed to be n,π*, and the degree of mixing with higher π,π* triplets should be minimized in the vapor phase. Furthermore, the results in Table I give evidence that energy transfer occurs from the carbonyl group. The quenching constants for benzil and benzophenone are much smaller than for their alkyl structural analogues, biacetyl and acetone, respectively. If electronic energy resides in the $^3n,\pi^*$ orbital, then the hard sphere collision diameter should be about 4.0 Å (sum of the van der Waals radii of C and O and the C=O bond length) in all aldehydes and ketones but will be about 8.0 Å in compounds such as benzophenone if energy migrates into the phenyl substituents. Hence, if all other factors controlling quenching efficiency remained constant, the quenching constants would be about four times larger for benzil and benzophenone than for biacetyl and acetone. Also, comparison of our quenching constants with literature values for the radiative decay constants, k_r, which may be determined from reported lifetimes and quantum yields of phosphorescence for acetone (180 s^{-1}, ref 13), biacetyl (84 s^{-1}, ref 14), benzaldehyde (420 s^{-1}, ref 15), acetophenone (120 s^{-1}, ref 16), and hexafluoroacetone (33 s^{-1}, ref 17), revealed no correlation. Since k_r can be used to estimate the degree of n,π^* character in an electronic state, this indicates that the trend in Table I is not directly related to the variation in the energy separation between and mixing of the lowest $^3n,\pi^*$ and $^3\pi,\pi^*$ states, as was suggested in ref 7.

With the exceptions of glyoxal, acetaldehyde, 1-indanone, and hexafluoroacetone the quenching constant is seen in Table I to increase with increasing triplet-state energy, which is opposite the trend observed in the quenching of the triplet state of aromatic hydrocarbons.[2,3] Furthermore, there is no deuterium effect in acetone, which, owing to its large T_1–S_0 energy gap, should have the largest deuterium effect of the compounds in Table I. These facts are inconsistent with a quenching mechanism controlled by Franck–Condon factors associated with harmonic, high-frequency vibrational modes, most notably C–H stretching modes,[18] and prompt a search for an alternate explanation.

The negative activation energies in Table II suggest the existence of weakly bound complexes, and, if quenching occurs through both reaction 1, energy transfer, and reaction 2, enhanced intersystem crossing, then k_q is expressed as

$$k_q = 1/9\,\frac{k_c k_{et}}{k_{-c} + k_{et}} + 1/3\,\frac{k_c k_{isc}}{k_{-c} + k_{isc}} \qquad (14)$$

Since there is no solvent cage in the vapor phase to stabilize the complex, it seems reasonable to assume that k_{isc}, $k_{et} \ll k_{-c}$, and eq 14 reduces to

$$k_q \simeq 1/9\frac{k_c k_{et}}{k_{-c}} + 1/3\frac{k_c k_{isc}}{k_{-c}} \ll {}^1\!/_9 k_c + {}^1\!/_3 k_c \qquad (15)$$

An inequality similar to k_{isc}, $k_{et} \ll k_{-c}$ has been found experimentally for other gas-phase complexes. For instance, in the case of complexes between triplet-state and ground-state benzene molecules k_{-c} is much greater than the rate constant for forward dissociation of the complex.[19]

It follows from eq 15 that

$$\ln k_q = -(\Delta G^\circ/RT) + \ln\,(k_{et}/9 + k_{isc}/3) \qquad (16)$$

Hence, all activation energies and the antiln of the intercepts, reported in Table II, correspond to free energies of stabilization of the complexes and the sum $k_{et}/9 + k_{isc}/3$, respectively. However, these are only relative values of $k_{et}/9 + k_{isc}/3$ since they are obtained from the intercepts of plots of ln k_q vs. 1/T, where k_q has units of a bimolecular rate constant, but k_{et} and k_{isc} have units of unimolecular rate constants. The comparable free energies of stabilization in Table II are not unexpected since O_2 apparently interacts with the carbonyl group of each molecule.

It should be noted that the only reported activation energy for quenching of the triplet state of a vapor-phase carbonyl-containing compound (to our knowledge), in this case acetone, was zero.[20] We can offer no explanation for the discrepancy with our corresponding activation energy. However, the quenching constants in ref 20 were determined over a more limited temperature range of 32–75 °C.

The ionization potentials for three of the four exceptions to the trend in Table I, namely, acetaldehyde, hexafluoroacetone, and glyoxal, are known to be much higher than those of the other compounds. This implies the possible importance of coupling between the excited state of the complex and a charge-transfer state.

Energies of charge-transfer states may be estimated with the expression

$$E_{CT} = I - EA - C \qquad (17)$$

in which I is the ionization potential of the carbonyl compound, EA is the electron affinity of oxygen, and C is the Coulomb stabilization energy of the complex. Literature values of I are listed in Table I, and EA is taken to be 0.67 eV.[21] C is not known for the complexes, but, since oxygen apparently always complexes to the carbonyl group, it seems reasonable that C will be relatively constant.

Values for I – EA are very large (8.4–11.0 eV) and would require Coulomb stabilization energies of about 5.4–8.0 eV to make the charge-transfer states isoenergetic with the carbonyl triplet states. These would be unusually large relative to typical Coulomb stabilization energies for charge-transfer complexes involving benzene derivatives, which range between 2.9 and 4.4 eV,[21,22] and, as is seen from eq 18, would require unusually short dipole lengths in the excited-state complex of 1.8–2.7 Å.

$$C = e^2/R = 14.14/R\ (\text{Å})\ \text{eV} \qquad (18)$$

R is the electrical length of the dipole, and it is assumed that the ground-state complex has no stabilization energy (see ref 21). Hence it appears that $E_{CT} > E_{T_1}$ for the compounds in Table I.

Further evidence for the existence of complexes comes from the absorption spectra in Figure 3. The presence of oxygen enhances the absorbance below 2400 Å, and the difference between absorbance spectra corresponds to the absorption spectrum of an acetone–oxygen complex. Although we were unable to determine the wavelength of maximum absorbance, the absorption spectrum of the complex appears to level off at wavelengths not too far below 2000 Å, and E_{CT} is estimated to be $\geq$6.20 eV, which is higher than E_{T_1}. From eq 17 the Coulomb stabilization energy is estimated to be $\leq$2.8 eV. The difference spectrum in a gaseous mixture of benzene and oxygen shows absorption in a similar wavelength range which has been attributed to a contact charge-transfer complex.[21]

Figure 4 gives evidence that the electronic state of the initially formed complex is coupled to a charge-transfer state. Kawaoka, Khan, and Kearns have shown that the rate constants for energy transfer and intersystem crossing in eq 1 and 2 can be expressed by an equation of the same form as eq 19 when the initial and

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(14) C. S. Parmenter and H. M. Poland, *J. Chem. Phys.*, **51**, 1577 (1969).

(15) Michael Berger, Irwin L. Goldblatt, and Colin Steel, *J. Am. Chem. Soc.*, **95**, 1717 (1973).

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(17) P. A. Hackett and K. O. Kutschke, *J. Phys. Chem.*, **81**, 1245 (1977).

(18) These results do not prove that Franck–Condon factors associated with distorted oscillators (modes), arising from the large geometry change that occurs upon electronic excitation of carbonyl-containing compounds, cannot control quenching. However, the trend in Table I would be fortuitous in this case.

(19) T. F. Hunter and M. G. Stock, *Chem. Phys. Lett.*, **22**, 368 (1973).

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(21) J. B. Birks, E. Pantos, and T. D. S. Hamilton, *Chem. Phys. Lett.*, **20**, 544 (1972). See references in this article for determinations of EA.

(22) (a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952); (b) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexen", Springer-Verlag, West Berlin, 1961; (c) G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

final states of the complex are coupled through a charge-transfer state.[23]

$$k_{\mathrm{et}},\, k_{\mathrm{isc}} = \frac{2\pi\rho F}{\hbar} \frac{|\langle\psi_{\mathrm{i}}|H|\psi_{\mathrm{CT}}\rangle\langle\psi_{\mathrm{CT}}|H|\psi_{\mathrm{f}}\rangle|^2}{(E_{\mathrm{CT}} - E_{\mathrm{T_1}})^2} \qquad (19)$$

F is the Franck–Condon factor for the transition and is different for k_{et} and k_{isc}. ρ is the density of states in the ground-state manifold of the carbonyl-containing compound at an energy, given by $E_{\mathrm{T_1}} - E_{\mathrm{O_2}}\ (^1\Sigma_g^+)$ or $E_{\mathrm{T_1}} - E_{\mathrm{O_2}}\ (^1\Delta_g)$ and $E_{\mathrm{T_1}}$ for k_{et} and k_{isc}, respectively, at which excess vibrational energy is dissipated. ψ_{i} and ψ_{f} are the states of the complex after it is formed initially and after it has passed through the charge-transfer state ψ_{CT}, respectively. ψ_{i} and ψ_{f} will be singlets and triplets in the cases of k_{et} and k_{isc}, respectively.

Equation 19 is strictly applicable to the unimolecular rate constants k_{et} and k_{isc} and not the bimolecular rate constant k_{q}. However, it is seen in Table II that the relative values of $k_{\mathrm{et}}/9 + k_{\mathrm{isc}}/3$ are approximately proportional to k_{q}. Since $k_{\mathrm{c}}/k_{-\mathrm{c}}$ is nearly constant, this implies that increases in k_{et} and k_{isc} account for the increase in k_{q} and gives justification for the application of eq 19 to k_{q}. Since the denominator of eq 19 is the same for both k_{et} and k_{isc}, k_{q} is plotted vs. $1/(I - \mathrm{EA} - E_{\mathrm{T_1}})^2$.

Figure 4 shows two distinct regions over which k_{q} increases, first gradually and then rapidly. The increase is consistent with eq 19 and gives evidence that quenching occurs by coupling of the initial state of the complex to a charge-transfer state. This may seem surprising in view of the fact that E_{CT} is apparently far above $E_{\mathrm{T_1}}$. However, Kawaoka et al. have found for aromatic triplets that the matrix elements for coupling the initial state, ψ_{i}, and the final state, ψ_{f}, to a charge-transfer state are several hundred times larger than a simple exchange matrix element which couples the initial and final states directly.[23] This could compensate for the energy barrier.

Since formation of a true charge-transfer complex is energetically disallowed, we are proposing that the initial state of the complex is only coupled to the charge-transfer state and that only partial charge separation exists in the complex. Hence the quenching mechanism may be represented by the equations

$$^3\mathrm{C} + \mathrm{O_2} \rightleftarrows [^1(\mathrm{C^*}\cdots\mathrm{O_2}) \rightleftarrows {}^1(\mathrm{C^{\delta+}}\cdots\mathrm{O_2}^{\delta-})^* \rightleftarrows {}^1(\mathrm{C}\cdots\mathrm{O_2}^*)] \xrightarrow{\mathrm{et}} \mathrm{C} + \mathrm{O_2}^* \qquad (20)$$

$$^3\mathrm{C} + \mathrm{O_2} \rightleftarrows [^3(\mathrm{C^*}\cdots\mathrm{O_2}) \rightleftarrows {}^3(\mathrm{C^{\delta+}}\cdots\mathrm{O_2}^{\delta-})^* \rightleftarrows {}^3(\mathrm{C}\cdots\mathrm{O_2})^*] \xrightarrow{\mathrm{isc}} \mathrm{C} + \mathrm{O_2} \qquad (21)$$

Further insight is obtainable from a comparison of k_{q} and k_{c}. Using a hard-sphere collision diameter of 3.7 Å (based on van der Waals radii) for collisions between $\mathrm{O_2}$ and $>\mathrm{C{=}O}$, those quenching constants in Table I which are less than $2.2 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ (set 1) are calculated to range between $\simeq 1/2200k_{\mathrm{c}}$ and $\simeq 1/53k_{\mathrm{c}}$. For the other molecules (set 2, comprised of acetone, acetaldehyde, indanone, and acetophenone) k_{q} in Table I is calculated to range between $\simeq 1/24k_{\mathrm{c}}$ and $\simeq 1/17k_{\mathrm{c}}$. This is perhaps a low estimate of the hard-sphere collision diameter, and the values of k_{q} may actually be smaller in relation to k_{c}.

It has been predicted that Franck–Condon factors should be much larger for quenching by energy transfer than by enhanced intersystem crossing in triplet-state aromatic hydrocarbons.[23] This has been extended to other molecules, and, since $k_{\mathrm{q}} \ll {}^1/_9k_{\mathrm{c}}$ in the lower region of Figure 4, process 20 is the dominant mechanism for molecules in set 1.

In the upper region of Figure 4 k_{q} increases much more rapidly and is no longer much less than ${}^1/_9k_{\mathrm{c}}$. Both facts suggest the onset or increased efficiency of another quenching path for molecules in set 2, which may be process 21. Since the Franck–Condon factor is expected to be much smaller for process 21 than for process 20, it must be the matrix elements coupling ψ_{i}, ψ_{CT}, and ψ_{f} that increase and cause the sharp increase in k_{q}. However, there seems to be no reason to expect these matrix elements to be larger for triplet-state complexes than for singlet-state complexes.

If the complexes in processes 20 and 21 were true charge-transfer complexes, then intersystem crossing between $^1(\mathrm{C^+}\cdots\mathrm{O_2}^-)^*$ and $^3(\mathrm{C^+}\cdots\mathrm{O_2}^-)^*$ could account for the large values of k_{q} for molecules in set 2. This explanation was used in ref 8 for molecules with large values of k_{q}. Hence, unless the gas-phase complexes $^1(\mathrm{C^{\delta+}}\cdots\mathrm{O_2}^{\delta-})^*$ and $^3(\mathrm{C^{\delta+}}\cdots\mathrm{O_2}^{\delta-})^*$ are somehow coupled, the most reasonable explanations for the large k_{q} values are that our estimates of k_{c} are too small or that the approximation k_{isc}, $k_{\mathrm{et}} \ll k_{-\mathrm{c}}$ is not true for molecules in set 2. In the former case k_{q} for all molecules could be much less than ${}^1/_9k_{\mathrm{c}}$ and would imply that process 20 is dominant, but this would not account for the rapid increase in the upper region of Figure 4. In the latter case no simple interpretation of the slopes and intercepts of the Arrhenius plots in Figure 3 could be given.

It is curious that the quenching rate for the aromatic hydrocarbons reported in ref 2 and 3, some of which have triplet-state energies in the same range as that reported here, is not also dominated by coupling to charge-transfer states since the ionization potentials of most of these compounds are less than those of the carbonyl-containing compounds. Apparently the delocalization of electron density in the $^3\pi^*$ orbital of an aromatic hydrocarbon molecule produces a small interaction with and small probability of electron transfer to the unfilled π_x or π_y orbitals of oxygen. On the other hand, the greater localization of electron density in the small $^3\pi^*$ orbital of a carbonyl group leads to greater interaction with and greater probability of electron transfer to oxygen. It is also possible, since separation of charge in the complex is important in coupling to a charge-transfer state, that the size of the dipole moment of the triplet state is important. Moreover, the dipole moments of several triplet state carbonyl-containing compounds are relatively large compared to the dipole moments of the $^3\pi,\pi^*$ state of aromatic hydrocarbons, which are approximately zero.[24,25]

Finally, a comparison of solution- and vapor-phase quenching constants is instructive. The quenching constants for the monocarbonyls, benzaldehyde, benzophenone, acetophenone, and indanone, differ by less than a factor of 2 for vapor- (Table I) and solution-phase systems.[7] On the other hand, the quenching constants for the dicarbonyls, biacetyl and benzil, are smaller by factors of 10 and 7, respectively, in the vapor phase than in solution.[7,26] These differences have two probable causes.

First, in dicarbonyl compounds the electron density of the π^* orbital is separated and localized on two carbonyl groups which are oriented with respect to each other at an angle between 0 and 180° about the interconnecting C–C bond. This separation of electron density reduces the overlap between the π^* orbital of dicarbonyls and the π_x and π_y orbitals of oxygen and makes energy transfer from the $^3\mathrm{n},\pi^*$ state less efficient for benzil and biacetyl than for monocarbonyl compounds.

Second, the low values of $E_{\mathrm{T_1}}$ make $E_{\mathrm{CT}} - E_{\mathrm{T_1}}$ substantially greater for biacetyl and benzil that for the monocarbonyl compounds. This makes the coupling between ψ_{i} and ψ_{f} smaller in biacetyl and benzil.

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These comments apply to molecules in both vapor and solution phases. However, owing to the solvent cage effect, in solution many collisions occur between oxygen and energy donor molecules during each encounter. This statistically increases the probability for energy transfer, compensates for the weaker coupling between ψ_i and ψ_{CT}, and makes the quenching constants comparable for all carbonyl and dicarbonyl compounds.

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Physical Binding of Tetraols Derived from 7,8-Dihydroxy-9,10-epoxybenzo[*a*]pyrene to DNA

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Abstract: The major reactive metabolite of the carcinogen *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (*anti*-BPDE) either reacts covalently with DNA or is hydrolyzed to the tetraol 7,8,9,10-tetrahydroxytetrahydrobenzo[*a*]pyrene (BPT). In this work it is shown that BPT binds noncovalently to DNA in aqueous buffer solution (5 mM sodium cacodylate buffer, pH 7.1) at 25 °C. This binding, at values of the binding ratio $r \approx 10^{-3}$, defined as the ratio of bound BPT molecules per DNA base, is characterized by two types of binding sites. Site I is characterized by a 10-nm red shift in the absorption spectrum (a shift from 343 to 353 nm for the most intense absorption band of BPT), a complete quenching of the fluorescence of BPT at this site, and a negative linear dichroism spectrum. These properties are characteristic of an intercalation-type complex, in which the BPT molecule is sandwiched between adjacent base pairs of DNA. Equilibrium dialysis and absorption and fluorescence spectroscopy are the techniques utilized to demonstrate that there is a second type of binding site (II). This binding site is characterized by the following: (1) no shift in the absorption spectrum with respect to that of free BPT molecules in the buffer solution; (2) unchanged fluorescence yield, decay time, and susceptibility to oxygen quenching. It is proposed that site II corresponds to an external type of binding site of BPT on the DNA molecule, and the similarity between this type of binding and that of the covalent adduct formed between *anti*-BPDE and DNA is noted. At the low values of r studied here ($^1/_{950}$–$^1/_{4700}$), the ratio of BPT molecules at sites I and II lies in the range of 2–4, while 16–38% of the total BPT molecules initially added remain free in solution.

Introduction

Carcinogenic polycyclic aromatic hydrocarbons (PAH) have been demonstrated to undergo metabolic conversion^{1} to reactive diol epoxide intermediates which bind covalently to nucleic acids in living cells. Benzo[*a*]pyrene, a ubiquitous environmental pollutant, has been most extensively studied, and *trans*-7,8-dihydroxy-*anti*-9,10-epoxy-7,8,9,10-tetrahydrobenzo[*a*]pyrene (*anti*-BPDE) has been strongly implicated by several lines of evidence as it ultimate carcinogenic form.$^{2-7}$ In particular, *anti*-BPDE has been identified as the principal metabolite of benzo[*a*]pyrene which binds to DNA in rodent, bovine, and human tissue. Binding occurs preferentially to guanine$^{7-9}$ and to a minor extent to adenine and to cytosine.^{10}

The reaction of *anti*-BPDE with DNA can be conveniently carried out in the laboratory,$^{9-12}$ and sufficient quantities of the complexes can be prepared for their physicochemical and biochemical characterization.$^{13-19}$

In aqueous solutions, *anti*-BPDE hydrolyzes to cis and trans tetraols (7,8,9,10-tetrahydroxytetrahydrobenzo[*a*]pyrene), a reaction which has been studied extensively.$^{20-23}$ The rate of decomposition of *anti*-BPDE to the benzo[*a*]pyrene tetraols (BPT) depends on the pH and on the other components present in the aqueous solution. In an effort to gain a better understanding of the mechanism of reaction between *anti*-BPDE and DNA, we have recently studied the kinetics of this reaction in aqueous solution at 25 °C utilizing absorption, fluorescence, and electric linear dichroism spectroscopic methods.^{24} It was found that the hy-

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