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Identification of Both Preequilibrium and Diffusion Limits for Reaction of Singlet Oxygen, $O_2(^1\Delta_g)$, with Both Physical and Chemical Quenchers: Variable-Temperature, Time-Resolved Infrared Luminescence Studies

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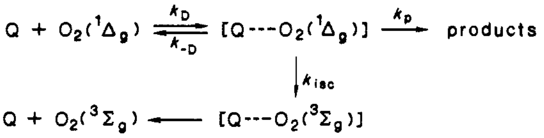
Abstract: The deactivation of singlet oxygen, $O_2(^1\Delta_g)$, by the quenchers β-carotene (β-C), strychnine (S), and 1,3-diphenylisobenzofuran (DPBF) has been examined over the temperature range −90 to +90 °C in toluene using time-resolved infrared luminescence spectroscopy. The aim of these experiments, to demonstrate that reactions of *both* physical and chemical quenchers proceed via the intermediacy of a reversibly formed $O_2(^1\Delta_g)$/quencher exciplex, has been achieved. The activation energy for diffusion-controlled reactions involving $O_2(^1\Delta_g)$ in toluene has been defined for the first time by demonstrating that, at low temperature, quenchings via three different mechanisms (electronic energy transfer, charge-transfer induced intersystem crossing, and cycloaddition to give endoperoxide) exhibit essentially identical Arrhenius slopes of 1.6–1.7 kcal mol^{-1}. At high temperature all three reactions deviate from the diffusion limit and in each case a second linear region is observed. Whereas the activation enthalpy corresponding to the high-temperature slope for β-C is positive (0.4 kcal mol^{-1}), those for S and DPBF are clearly negative. These results provide compelling evidence that the balance between physical and chemical quenching in organic and biological systems is a function of competition between exciplex photophysics and exciplex photochemistry. These data have led to the conclusion that in no cases of quenching hitherto examined in terms of activation parameters, e.g., those of simple alkenes, enol ethers, indoles, and cyclic dienes, can exciplex formation be rate-limiting. Control experiments with 2,3-dimethylbut-2-ene (DMB) and its perdeuterio analogue (DMB-$^2H_{12}$) are in agreement with this conclusion.

I. Introduction

The quenching of singlet oxygen, $O_2(^1\Delta_g)$, by organic/biological substrates has been a subject of major research effort over the last two decades.[1] Such quenching may be physical or chemical in nature and in living systems would correspond to biological protection or biological damage, respectively. The mechanistic aspects of such reactions, both experimental and theoretical, have recently been thoroughly reviewed.[2] It was concluded that charge-transfer (CT) interactions are of critical importance and that, in many cases, chemical reaction proceeds via an exciplex and/or zwitterionic species. It was also concluded that exciplex formation was *rate determining*. However, the *experimental* findings[3] cited in support of exciplex involvement—(a) rate constants which are orders of magnitude down on that for diffusion, (b) activation enthalpies close to zero or even negative, and (c) highly negative activation entropies—are characteristic of reactions of an exciplex which is formed *rapidly* and *reversibly*.[4] It has therefore been recently proposed[3e] that reactions of $O_2(^1\Delta_g)$ in general proceed via a mechanism summarized in Scheme I for a substrate Q. Time-resolved experiments involving exciplexes most commonly involve the use of single photon counting to monitor the emission from monomer and/or exciplex singlet states, generally over not more than a few tens of nanoseconds. The changes in concentration with time are governed by a pair of coupled ordinary differential equations.[5] However, the lifetime of $O_2(^1\Delta_g)$, $\tau_\Delta = k_d^{-1}$, is several orders of magnitude longer than those of such singlet states. This fact, together with the use of suitable quencher concentrations (vide infra), ensures that $k_d + k_D[Q] \ll k_{-D} + (k_{isc} + k_p)$; cf. Scheme I. This simplifies the kinetics to the extent that the relationships of eq 1 and 2 hold

Scheme I



$$k' = k_d + k_q[Q] \tag{1}$$

$$k_q = \frac{k_D\,(k_{isc} + k_p)}{k_{-D} + (k_{isc} + k_p)} \tag{2}$$

where k' is the first-order constant for decay of $O_2(^1\Delta_g)$ and k_q is the overall quenching rate constant.[6,7] For fast ($k_{-D} \ll k_p + k_{isc}$) and slow ($k_{-D} \gg k_p + k_{isc}$) quenchers this reduces to eq 3 (diffusion limit) and 4 (preequilibrium limit), respectively, where

$$k_q = k_D \tag{3}$$

$$k_q = K(k_{isc} + k_p) \tag{4}$$

K is the equilibrium constant for exciplex formation. There is no doubt that, given this mechanism, the vast majority of the host

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(7) Exciplex kinetics are strictly analogous to those for reversible triplet energy transfer, for which the necessary mathematical model was first introduced.[6a] In fact, the exciplex quenching of $O_2(^1\Delta_g)$ is more closely related kinetically to the reversible quenching of biacetyl phosphorescence by triplet energy acceptors[6a] than to the classical exciplex systems.

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of k_q's determined at room temperature (cf. ref 8) would correspond to the preequilibrium situation of eq 4. In such a situation the zero or even negative experimental enthalpies of activation, $\Delta H^{\ddagger}_{exp}$, represent a balance between a negative ΔH° for exciplex formation and the positive activation enthalpy for consummation of quenching, $\Delta H^{\ddagger}_{isc}$(physical) or $\Delta H^{\ddagger}_{p}$(chemical).[3c,e] The only other circumstantial evidence in favor of the mechanism of Scheme I comes from a variable-temperature study on vitamin E quenching of $O_2(^1\Delta_g)$ which shows that positive Arrhenius slopes (negative $\Delta H^{\ddagger}_{exp}$; preequilibrium limit) become less positive as the temperature is lowered.[3e]

In the work to be described we have addressed ourselves to the problem of providing conclusive evidence for the mechanism discussed above by accurately defining both preequilibrium *and* diffusion limits for singlet oxygen quenching. It appeared that success in such a goal would depend on a number of basic criteria.

(a) It was imperative that any individual quenching process examined be exclusively physical or chemical in nature and that a chemical process should lead exclusively to one product. This would avoid problems resulting from sums of rate constants (cf. eq 4), each with varying temperature sensitivities.

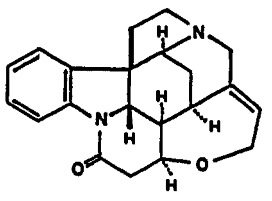
(b) Room-temperature quenching rate constants would have to be relatively high so that the lowering of k_{-D} with temperature could, in fact, allow the diffusion limit to be attained.[9]

(c) A solvent with a wide liquid temperature range would be required. Nevertheless, it might not be possible to cover the whole of the mechanistically significant temperature range, and examination of more than one quencher of a particular type might therefore be of value.

(d) An independent control of the diffusion limit for reactions involving $O_2(^1\Delta_g)$ was required.

(e) If it could be shown that both an exclusively physical and an exclusively chemical quencher operate via rapid and reversible exciplex formation, it would only be a small intellectual jump to the conclusion that substrates which quench both physically and chemically do so by partition from the exciplex as shown in Scheme I.

Work based on the above considerations leads us to describe here experiments on the quenching of $O_2(^1\Delta_g)$ in toluene by the compounds strychnine (S; **1**), 1,4-diazabicyclo[2.2.2]octane (DABCO; **2**), 1,3-diphenylisobenzofuran (DPBF; **3**), and β-carotene (β-C) using time-resolved infrared emission spectroscopy. Both S[11] and DABCO[12] are exclusively physical quenchers of $O_2(^1\Delta_g)$ as a consequence of their rigid σ frameworks; DPBF is exclusively a chemical quencher leading to a single primary product.[13] Since, even at room temperature, β-C quenches at a close-to-diffusion-controlled rate,[14] via triplet energy transfer, this molecule was chosen as a standard for defining the diffusion limit.



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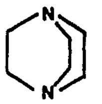

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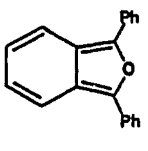

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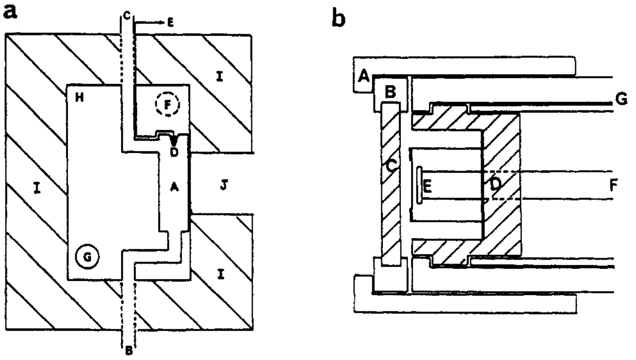

Figure 1. (a) Variable-temperature, time-resolved infrared luminescence detection system: (A) flow-through cell, (B) solution inlet, (C) solution outlet, (D) well containing thermocouple and zinc oxide paste, (E) connection of thermocouple to electronic thermometer, (F) cooled nitrogen gas inlet, (G) cooled nitrogen gas outlet, (H) aluminum heat sink, (I) expanded polythene insulation, (J) diode housing [see (b)]. (b) Expanded plan of diode housing: (A) PVC end-cover, (B) aluminum holding ring, (C) silicon filter, (D) PTFE insert, (E) germanium diode, (F) connections to amplifier, (G) concentric, cylindrical, anodized brass tubes.

The results of this work allow conclusions to be drawn concerning $O_2(^1\Delta_g)$ quenching reactions which are relatively inefficient. For comparative purposes we have therefore examined the rate and activation characteristics for chemical reaction of $O_2(^1\Delta_g)$ in toluene with 2,3-dimethylbut-2-ene (DMB; **4**) and its perdeuterio analogue (DMB-$^2H_{12}$).

2. Experimental Section

Time-resolved experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, using a J K Lasers System 2000 Nd:YAG laser. The laser beam was unfocused and attenuated by means of wire mesh filters. Incident energies were 1–2 mJ per pulse.

2.1. Variable-Temperature Infrared Luminescence Experiments. The flow-through cell was constructed from a standard silica fluorescence cuvette, a well sunk into the shoulder accommodating a copper/Constantan thermocouple which was connected to a Comark electronic thermometer. The cell was housed in a variable-temperature box (Figure 1) which was a modified version of a published design.[15] Because of the necessity for the germanium diode detector to be close-coupled to the source of luminescence, the cell was not housed centrally but with the "detection face" flush with the edge of the aluminum heat sink, good thermal contact being achieved with a zinc oxide-based preparation. The heat sink was drilled to accommodate two cylindrical cartridge heaters, connected in series to a Variac serving as a heating rate control. A channel drilled from front to back allowed passage of dry precooled nitrogen gas through the block, over the cell, and out via a copper pipe at the heat sink base. The cooling rate was controlled by gas flow. A retractable barrel-shaped housing allowed close-coupling of the reaction cell and the detector, a 5-mm^2 Electro-Optical Systems Specialists Inc. G-050 germanium diode. The latter was separated from the cell face by a silicon filter which excluded emission below 1100 nm and any stray laser light. The end cover which served to retain the silicon filter was constructed of PVC to prevent heat transfer to and from the heat sink. The laser light entry port consisted of an evacuated double-walled quartz disk, surrounded by expanded polyethylene and insulated from the reaction cell by a drilled block of PTFE. The flow of dry nitrogen prevented condensation on either the reaction cell or the silicon filter. The output from the diode, with a small reverse bias voltage, was led via a 200-Ω load resistance to the input of a Tektronix 7A22 differential amplifier. In more recent experiments the 7A22 has been replaced by a

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[9] That such a possibility was feasible, at least in principle, was demonstrated by the fact that, for α-cyanonaphthalene/olefin[10a] and anthracene/amine[10b] exciplex systems, a decrease in temperature of 40 °C can lead to a 10–50-fold decrease in k_{-D} but only an ~2-fold decrease in the sum of the rate constants for natural decay of the exciplex.

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Table I. Rate Constants (at RT), k_q/L mol^{-1} s^{-1}, and Activation Parameters (at RT), $\Delta H^{\ddagger}_{exp}$/kcal mol^{-1} and $\Delta S^{\ddagger}_{exp}$/cal mol^{-1} K^{-1}, for Quenching of $O_2(^1\Delta_g)$ in Toluene[a]

		preequilibrium limit		diffusion limit	
quencher	k_q	$\Delta H^{\ddagger}_{exp}$	$\Delta S^{\ddagger}_{exp}$	$\Delta H^{\ddagger}_{exp}$	$\Delta S^{\ddagger}_{exp}$
β-C	1.1×10^{10}[b]	0.4 ± 0.3	-14.3 ± 0.5	1.1 ± 0.3	-12.0 ± 1.4
S	9.3×10^{8}[c]			1.0 ± 0.3	-18.4 ± 1.6
DABCO	2.1×10^{8}[c]	-1.6 ± 0.3	-30.0 ± 1.2		
DPBF	8.9×10^{8}[d]	-1.3 ± 0.2	-25.9 ± 0.6	1.0 ± 0.3	-16.6 ± 1.2
DMB[e]	3.6×10^{7}	-0.74 ± 0.11	-30.1 ± 0.5		
DMB-$^2H_{12}$	3.2×10^{7}	-0.65 ± 0.11	-30.1 ± 0.4		

[a] Quoted errors are based on an error of ±5% for rate constants determined at a given temperature. [b] The published value for benzene, determined by an indirect time-resolved method = 1.3×10^{10} L mol^{-1} s^{-1}.[14a] [c] These values have previously been reported.[11] [d] Published values, determined by indirect time-resolved techniques, vary from 6.6 to 9.4×10^{8} L mol^{-1} s^{-1}.[3c,16] [e] Previously reported values for $\Delta H^{\ddagger}_{exp}$ and $\Delta S^{\ddagger}_{exp}$ in CS_2 are 0.5 kcal mol^{-1} and −26 cal mol^{-1} K^{-1}.[3b]

Table II. Activation Energies, E_a/kcal mol^{-1}, and Preexponential Factors, A/L mol^{-1} s^{-1}, for Quenching of $O_2(^1\Delta_g)$ in Toluene[a]

	preequilibrium limit		diffusion limit	
quencher	E_a	A	E_a	A
β-C	1.0 ± 0.3	$(8.0 \pm 1.7) \times 10^{10}$	1.7 ± 0.3	$(3.1 \pm 1.9) \times 10^{11}$
S			1.6 ± 0.3	$(1.3 \pm 0.9) \times 10^{10}$
DABCO	-1.0 ± 0.3	$(3.3 \pm 1.7) \times 10^{7}$		
DPBF	-0.7 ± 0.2	$(2.4 \pm 0.7) \times 10^{8}$	1.6 ± 0.3	$(2.9 \pm 1.5) \times 10^{10}$
DMB	-0.14 ± 0.11	$(2.9 \pm 0.7) \times 10^{7}$		
DMB-$^2H_{12}$	-0.05 ± 0.11	$(3.0 \pm 0.7) \times 10^{7}$		

[a] See footnote *a* in Table I.

Judson Model 100 preamplifier coupled to a Tektronix 7A13 differential comparator. The overall rise time (0–67%) was 500 ns. Oxygen-saturated solutions, changed automatically by oxygen pressure after each shot, were considered to be equilibrated after a steady temperature (±0.1 °C) had been maintained for 1 min. The rate constant for sensitizer triplet decay, monitored by kinetic absorption spectrometry, was in all cases $\geq 1.0 \times 10^{7}$ s^{-1}. Since the observed rate constant for $O_2(^1\Delta_g)$ emission decay was in all cases $\leq 1.3 \times 10^{5}$ s^{-1}, the formation of the latter species did not perturb its subsequent decay profile. The rate constants listed in Table I were determined at room temperature (22.5 °C) with aerated solutions. In these cases sensitizer triplet and $O_2(^1\Delta_g)$ decay constants were 3.3×10^{6} and $\leq 1.6 \times 10^{5}$ s^{-1}, respectively. All decay profiles were strictly exponential. The low $O_2(^1\Delta_g)$ decay constants ensured the validity of eq 1 and 2 (cf. ref 6).

2.2. Purification Procedures. Toluene (AnalaR, BDH) was refluxed over lithium aluminum hydride for 48 h and fractionally distilled through a 4-ft steel-wool-packed column. 2-Acetonaphthone (Aldrich) was recrystallized from ethanol. β-Carotene (Fluka) was recrystallized from toluene/methanol before use. 1,4-Diazabicyclo[2.2.2]octane (BDH) was recrystallized from absolute ethanol and sublimed twice (65 °C; 0.2 torr) before use. 1,3-Diphenylisobenzofuran (Aldrich) and protoporphyrin IX dimethyl ester (Fluka) were used as received. Strychnine (BDH) was twice recrystallized from absolute ethanol.

2.3. Synthetic Procedures. DMB-$^2H_{12}$. This material was prepared according to the published method[17] in 41% yield. Material thus produced had a chemical purity of >99.5% by GLC (10% SP1000 on Chromosorb W HP 80–100 mesh; 2.7 m × 4 mm (i.d.); 78 °C; 200 psi) and an isotopic purity of 99% (electron impact mass spectrum).

DMB. Commercial samples of this material could not be purified to the standard of the above synthetic DMB-$^2H_{12}$ as determined from $O_2(^1\Delta_g)$ quenching rate constants. The above synthesis was therefore repeated with nondeuterated materials.

3. Results

3.1. General Considerations. The use of time-resolved infrared emission spectroscopy to monitor the lifetime of $O_2(^1\Delta_g)$ in solution is now well-documented.[18] We have employed this technique to determine rate and activation parameters for the $O_2(^1\Delta_g)$ quenchers listed in Tables I and II. Toluene was chosen as solvent because of its wide liquid range, −93 to 111 °C, at atmospheric pressure. For the experiments with S, DABCO, β-C, DMB, and DMB-$^2H_{12}$, the $O_2(^1\Delta_g)$ was produced by pulsed laser (12 ns) excitation at 355 nm of 2-acetonaphthone in aerated or oxygenated toluene. Because of the high light sensitivity of DPBF, experiments with this quencher were performed via excitation at 532 nm of protoporphyrin IX dimethyl ester in the same medium. A specially constructed variable-temperature box (section 2.1) allowed the requisite close-coupling of detector and flow-through reaction cell and access to a temperature range of nearly 200 °C.

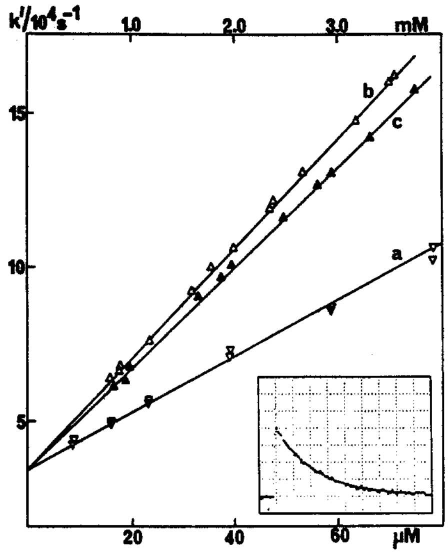

Figure 2. First-order constant for decay of $O_2(^1\Delta_g)$ emission at 22.5 °C, k', as a function of quencher concentration: (a) DPBF (lower abscissa), (b) DMB, and (c) DMB-$^2H_{12}$ (upper abscissa). Inset: time-dependence, with first-order fit, of emission decay following pulsed laser excitation at 532 nm (0.94 mJ) of protoporphyrin IX dimethyl ester ($OD_{532} = 0.2$) in oxygenated toluene containing DPBF (7.9×10^{-6} mol L^{-1}); 10 µs/div, 10 mV of deflection/div, $k' = 4.4 \times 10^{4}$ s^{-1}.

3.2. Rate Parameters. Pulsed laser excitation of either 2-acetonaphthone (355 nm; $OD_{355} = 0.5$; 2.9×10^{-3} mol L^{-1}) or protoporphyrin IX dimethyl ester (532 nm; $OD_{532} = 0.2$; 3.6×10^{-5} mol L^{-1}) in aerated toluene resulted in $O_2(^1\Delta_g)$ formation via the usual channels within 300 ns.[19] Subsequent decay of

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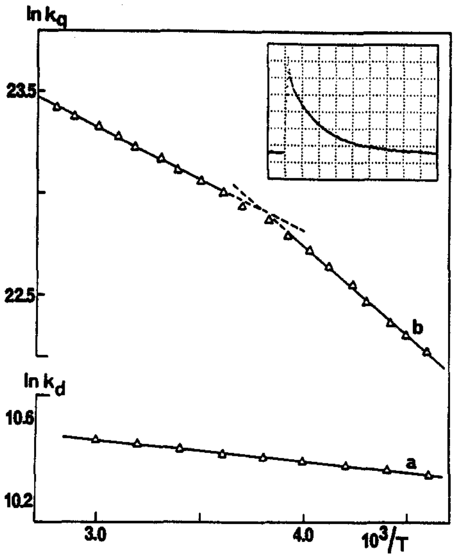

Figure 3. Arrhenius plots for (a) the natural decay constant, k_d, for $O_2(^1\Delta_g)$ in toluene and (b) the rate constant, k_q, for quenching of $O_2(^1\Delta_g)$ by β-C in the same solvent. Inset: time-dependence, with first-order fit, of $O_2(^1\Delta_g)$ emission decay following pulsed laser excitation at 355 nm (1.13 mJ) of 2-acetonaphthone (OD_{355} = 0.5) in oxygenated toluene containing β-C (3.3×10^{-6} mol L^{-1}) at −46 °C; 10 μs/div, 20 mV of deflection/div, $k' = 5.2 \times 10^4$ s^{-1}.

$O_2(^1\Delta_g)$ luminescence at 1267 nm corresponded to a lifetime, $\tau_\Delta = k_d^{-1}$ (eq 5), of 29 μs, in excellent agreement with published

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g) \quad (5)$$

values.[18a,b,20] Determination of the first-order rate constant for $O_2(^1\Delta_g)$ decay, k', as a function of added quencher, Q (eq 6),

$$O_2(^1\Delta_g) + Q \xrightarrow{k_q} \text{loss of } O_2(^1\Delta_g) \quad (6)$$

allowed determination of quenching rate constants at room temperature according to eq 1. Typical plots are shown in Figure 2 and rate constants together with literature data are listed in Table I.

3.3. Activation Parameters. 3.3.1. Natural Decay of $O_2(^1\Delta_g)$. Determination of k_d over the temperature range −70 to 60 °C yielded a linear and reproducible Arrhenius plot (Figure 3a). The thus determined activation energy, 0.2 kcal mol^{-1}, corresponded to a $\Delta H^{\ddagger}_{exp}$ value of −0.4 kcal mol^{-1} at room temperature. To date, published effects of temperature on k_d have been relatively rare.[3a,21,22] The most accurate data are those for acetone using the time-resolved emission technique.[22] The lack of observation of a temperature effect on k_d over a 100 °C temperature range is in agreement with our findings concerning toluene.

3.3.2. Quenching by β-C. In order to determine the effect of temperature on k_q for each quencher, k' (cf. eq 1) was determined over the temperature range −90 to 90 °C for (a) a solution containing sufficient quencher to increase k' by a factor of ~3 relative to k_d and (b) a "blank" solution containing no quencher. Subtraction of the resulting k' and k_d versus temperature plots yielded a k_q[Q] versus temperature relationship which, after correction for concentration changes as a consequence of solvent density dependence on temperature, allowed construction of the Arrhenius plot for k_q.

In Figure 3b is shown the plot for β-C, and clearly two linear regions are observed corresponding at high and low temperature to activation energies of 1.0 and 1.7 kcal mol^{-1}, respectively (Table II). Three points are worth emphasizing.

(a) Because it is a particularly fast quencher, β-C was chosen to give us the best chance of defining the diffusion limit. This clearly appears to have been successful at low temperature and has been confirmed (vide infra).

(b) The change of slope in the region of −10 °C reflects progression from the diffusion limit to the preequilibrium limit. However, in contrast to the quenchers discussed in the following sections, the relatively weak binding within the intermediate complex results in a balance between $\Delta H°$ and $\Delta H^{\ddagger}$ for energy transfer which is just positive (Table I). It has been known for some time that $O_2(^1\Delta_g)$ and $^3\beta$-C* are approximately isoenergetic,[23] but this is the first indication, as far as we are aware, that $^3\beta$-C* lies somewhat above $O_2(^1\Delta_g)$.

(c) The low-temperature slope of Figure 3b corresponds to a rate constant at room temperature of 1.3×10^{10} L mol^{-1} s^{-1} (cf. values given in Table I). This is a factor of 2–3 lower than rate constants for the oxygen-induced intersystem crossing of electronically excited singlet states in toluene[24] and has been attributed to an orbital statistical factor of 0.5 arising out of the degeneracy of the $O_2(^1\Delta_g)$ state.[25,26]

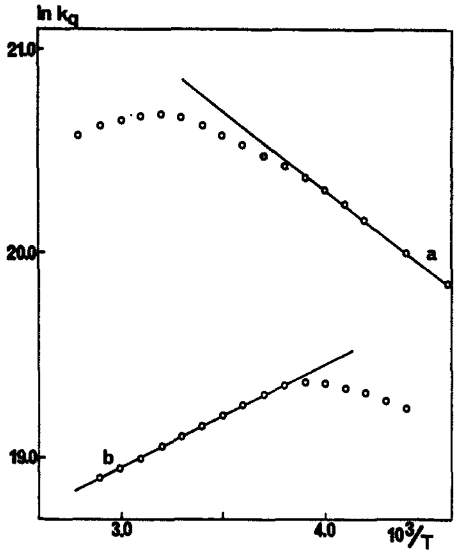

Figure 4. Arrhenius plots for the rate constants, k_q, for quenching of $O_2(^1\Delta_g)$ in toluene by (a) S and (b) DABCO.

3.3.3. Quenching by S. In Figure 4a is shown the corresponding Arrhenius plot for S using 2-acetonaphthone as the $O_2(^1\Delta_g)$ sensitizer. A linear region corresponding to an activation energy of 1.6 kcal mol^{-1} is clearly visible at low T. This value is identical within experimental error with that determined at low T for β-C (Figure 3b; Tables I and II). In contrast to the β-C plot, that for S clearly inverts in the region of room temperature and gives a positive slope at high temperature, in clear agreement with a change from the diffusion limit to the preequilibrium limit. However, the available temperature range did not allow clear definition of a linear region at high temperature for this quencher. We have been able to identify such a region for the physical quencher DABCO as shown below.

3.3.4. Quenching by DABCO. Given the considerations outlined in Scheme I and eq 1–3, a *slower* quencher of the *same type* as S would be expected to undergo inversion from the diffusion limit to the preequilibrium limit at a lower temperature than does S. This would not be the case in general because whether one

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(20) Salokhiddinov, K. I.; Byteva, I. M.; Gurinovich, G. P. *J. Appl. Spectrosc.* **1981**, *34*, 561.

(21) Long, C. A.; Kearns, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 2018.

(22) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.

(23) (a) Land, E. J.; Sykes, A.; Truscott, T. G. *Chem. Commun.* **1970**, 332. (b) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244. (c) Herkstroeter, W. G. *Ibid.* **1975**, *97*, 4161.

(24) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455.

(25) Stevens, B. *J. Photochem.* **1974/75**, *3*, 393.

(26) A referee has raised the possibility that the exciplex reactivity of each quencher examined in this work is influenced by an orbital statistical factor.[25] While this would in no way affect the conclusions of this work (vide infra), it should be emphasized that the said orbital statistical factor was proposed on the basis of a transition state for reaction of $O_2(^1\Delta_g)$ with anthracene which had the symmetry characteristics of the endoperoxide product. Of the quenchers examined in this work only the reactivity of DPBF is clearly comparable. For instance, in the case of S, an "end-on" exciplex in which nitrogen and the oxygen molecule were colinear would clearly not be subject to such an orbital statistical factor.

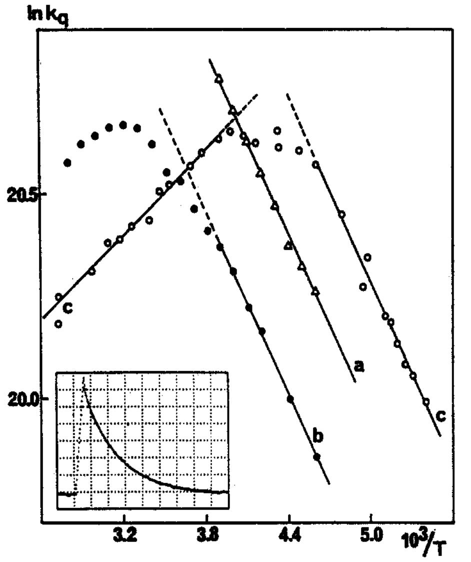

Figure 5. Arrhenius plots for the rate constants, k_q, for quenching of $O_2(^1\Delta_g)$ in toluene by (a) β-C (minus two natural logarithm units for comparative purposes), (b) S, and (c) DPBF. Inset: time-dependence, with first-order fit, of $O_2(^1\Delta_g)$ emission decay following pulsed laser excitation at 532 nm (2.3 mJ) of protoporphyrin IX dimethyl ester (OD_{532} = 0.2) in oxygenated toluene containing DPBF (1.07×10^{-4} mol L^{-1}), at -77 °C; 5 μs/div, 20 mV of deflection/div, $k' = 1.0 \times 10^5$ s^{-1}.

quencher is "faster" or "slower" than another could well depend on the temperature at which the quenching rate constants were measured (vide infra). In Figure 4b is shown the Arrhenius plot for DABCO in toluene, again using 2-acetonaphthone as $O_2(^1\Delta_g)$ sensitizer. Unfortunately, DABCO began to crystallize out of the toluene at temperatures below -50 °C, and a dependable linear low-temperature region could not be achieved, although clearly the plot of 4b appears to be approaching the slope corresponding to diffusion control. At about -20 °C inversion to the preequilibrium limit takes place and a clearly linear high-temperature region with an activation energy of -1.0 kcal mol^{-1} is apparent.

3.3.5. Quenching by DPBF. It is perhaps appropriate that DPBF, a molecule whose bleaching by $O_2(^1\Delta_g)$ in the time-resolved mode has allowed several breakthroughs in the understanding of $O_2(^1\Delta_g)$ properties[3a,c,e,16,23b,27] in the past, should prove the ideal substrate in work based on time-resolved IR emission spectroscopy, the technique which has replaced the aforementioned bleaching method. As mentioned (section 3.1) DPBF is light-sensitive. Such sensitivity is of no consequence when $O_2(^1\Delta_g)$ is produced by porphyrin excitation at 532 nm. In Figure 5 is shown the Arrhenius plot for DPBF quenching, together with those for S and β-C (low temperature region) for comparative purposes. Points to be emphasized are as follows.

(a) The DPBF plot undergoes inversion at -30 to -40 °C from the diffusion limit to the preequilibrium limit. The ideal consequence of this fact is that clear definition of linear regions at both high and low temperature is possible.

(b) The slope of the linear region at low temperature is identical, within experimental error (cf. Tables I and II), with those of S and β-C, thus providing further confirmation that this corresponds to diffusion control.

(c) The slope of the linear region at high temperature, E_a = -0.7 kcal mol^{-1}, $\Delta H^{\ddagger}_{exp} = -1.3$ kcal mol^{-1} at room temperature, clearly is in agreement with the preequilibrium situation.

(d) The relative vertical positions of the low-temperature plots for β-C, S, and DPBF are obviously determined by the preexponential factors (Table II). There appears to be a significant difference in that the value for β-C is an order of magnitude higher than for S and DPBF. This is not unreasonable in that a process involving triplet energy transfer to an extended polyene would be expected to have less demanding collision orientation requirements than quenching processes requiring binding interaction at specific sites (see also ref 26).

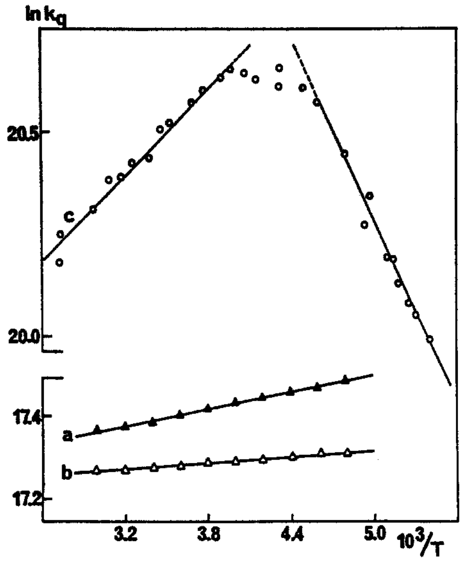

Figure 6. Arrhenius plots for the rate constants, k_q, for quenching of $O_2(^1\Delta_g)$ in toluene by (a) DMB, (b) DMB-$^2H_{12}$, and (c) DPBF.

(e) The significance of the inversion temperatures for S and DPBF is difficult to assess because differences in the values of k_{isc} and k_p (cf. eq 2-4) may be masked by variation in k_{-D} as a consequence of differences in exciplex binding.

(f) It is of interest that, although S and DPBF were chosen as substrates because they are "fast" quenchers with essentially the same k_q at room temperature (cf. Table I), they are, in fact, mechanistically distinct at that temperature in that DPBF is clearly at the preequilibrium limit, S much closer to the diffusion limit.

3.3.6. Quenching by DMB and DMB-$^2H_{12}$. In Figure 6 are shown the Arrhenius plots for the above alkenes in toluene together with that for DPBF for comparative purposes. The strictly linear nature of the plots for the olefins clearly indicates the absence of a change in the rate-determining step with temperature, and comparison with DPBF (Figure 6; Tables I and II) shows that *rate-determining* exciplex formation is not involved. The data are, however, in good agreement with rapid, reversible exciplex formation in the preequilibrium situation. In addition an important conclusion, at least within the limits of the accuracy of our data, is that the isotope effect, k_H/k_D = 1.1 at room temperature (Figure 2; Table I), is a consequence of enthalpy as opposed to entropy factors, at least in toluene.

4. Conclusions

The results herein described provide compelling evidence that the reaction of $O_2(^1\Delta_g)$ with both S and DPBF proceeds via the rapid and reversible formation of an intermediate.[28] The great similarity (Figure 5) in the behavior of these two quenchers,

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[27] (a) Adams, D. R.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 586. (b) Young, R. H.; Brewer, D.; Keller, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 375.

[28] In two theoretical papers[29] it has been claimed that calculations show that, for carbene addition to olefins, a negative activation energy is sometimes associated with reversible intermediate formation, sometimes not. We mention this here because carbene and singlet oxygen reactions exhibit somewhat similar rate and activation parameters.[3,30] However, the current discussion centers around the reactions of two quenchers which mechanistically could not behave more differently, one (S) involving a charge-transfer induced intersystem crossing process and one (DPBF) a highly ordered six-center transition state leading to an endoperoxide. We are therefore forced to conclude that in these cases reversible intermediate formation is a fact, in keeping with a wealth of photochemical precedent.[4,10]

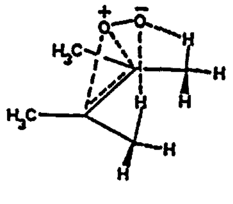
[29] (a) Houk, K. N.; Rondan, N. G.; Mareda, J. *J. Am. Chem. Soc.* **1984**, *106*, 4291. (b) Houk, K. N.; Rondan, N. G. *Ibid.* **1984**, *106*, 4293.

[30] (a) Giese, B.; Meister, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 595. (b) Giese, B.; Lee, W.-B.; Meister, J. *Justus Liebigs Ann. Chem.* **1980**, 725. (c) Wong, P. C.; Griller, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1981**, *103*, 2423. (d) Giese, B.; Lee, W.-B. *Chem. Ber.* **1981**, *114*, 3306. (e) Turro, N. J.; Lehr, G. F.; Butcher, J. A.; Moss, R. A.; Guo, W. *J. Am. Chem. Soc.* **1982**, *104*, 1754. (f) Giese, B.; Lee, W.-B.; Neumann, C. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 310.

together with the fact that quenching by S leads to no chemical product, provides strong evidence that this intermediate is an exciplex. Exciplexes are relatively highly ordered species which may exhibit $\Delta S°$ values as highly negative as −25 cal mol^{-1} K^{-1};[10] their formation is therefore dependent on favorable enthalpy factors. Reaction takes place at every collision which has the correct geometry, typical activation entropies being −10 to −15 cal mol^{-1}, K^{-1}.[10] In the case of S and DPBF the corresponding values (Table I) reflect a somewhat more demanding orientation requirement. There is no reason to believe that, for exciplex formation between $O_2(^1\Delta_g)$ and other organic quenchers, entropy factors should be significantly more demanding than for S and DPBF. Therefore exciplex formation can only become significantly slower, i.e., by orders of magnitude, as a consequence of a major increase in the *enthalpy* of activation. For quenchers with an overall quenching rate constant of 10^7–10^3 L mol^{-1} s^{-1} this would correspond to an activation enthalpy of 3.5 to 9 kcal mol^{-1}, for an activation entropy of −20 cal mol^{-1} K^{-1} at room temperature (cf. Table I). Since experimental values for such quenchers are 0 ± 2 kcal mol^{-1},[3] it is absolutely clear that exciplex formation can never be rate determining in such cases. This conclusion is, of course, simply in accord with accepted facts concerning exciplex properties. As exciplex stability *decreases*, e.g., when the ionization potential of an electron-donating quencher increases, the rate constant for dissociation, k_{-D}, *increases* until a limiting situation is reached, i.e., that where collision leads simply to an encounter complex whose rate constant for dissociation is governed solely by diffusion parameters. Thus, two key conclusions come from the above considerations.

(a) Quenching for which exciplex formation is rate-limiting must be "fast". This point is amply illustrated by Figures 4, 5, and 6. (b) Quenching which is "slow" must proceed either (i) via a rapidly and reversibly formed exciplex followed by a subsequent slow step or (ii) simply via a slow step involving no intermediate other than the rapidly and reversibly formed encounter complex. It should be possible to distinguish between these two situations since, in the former case, one might anticipate an experimental activation enthalpy significantly less than that for diffusion, but probably less negative than that for the faster quenchers. In the latter case activation enthalpies at least as high as that for diffusion in the particular solvent would be anticipated. The data for DMB and DMB-$^2H_{12}$ in toluene (Figure 6) clearly demonstrate that these olefins come into the former category.

Given that it is not logical to conclude that a "slow" quencher, such as an olefin, could react via a highly ordered exciplex which is formed *irreversibly*, it is equally difficult to argue that an even *more highly* ordered *irreversibly formed* complex could lie further along the reaction coordinate leading to product than does the exciplex.[3b,31] Common sense demands that the next maximum on the free energy profile after the exciplex is the transition state for irreversible formation of product. This conclusion appears in direct contrast to the highly ordered and *irreversibly* formed intermediate complex of type **5** proposed by Stephenson,[31] and adopted by others,[3b,32] to explain the small but significant deuterium isotope effect (k_H/k_D = 1.38–1.41) witnessed for the deuterated DMB (**7**) relative to that for **8** (k_H/k_D = 1.05–1.09) in deuterated acetone.[33] Although we have no *detailed* alternative rationale for these admittedly small effects, we would emphasize that a transition state for allylic hydroperoxide formation lying somewhere between **5** and a standard chair transition state (**6**) would be influenced energetically by several distinct factors, hitherto not considered. These could result in a reinforcing or cancelling of individual small contributions to an overall isotope effect depending on the relative orientation of CH_3/CD_3 groups. Such factors are summarized below.



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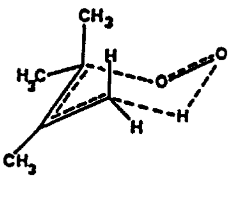

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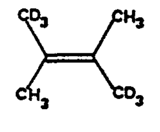

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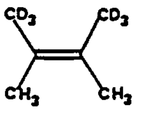

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(a) CD_3 has a smaller van der Waals' radius than does CH_3.[34] In crowded molecules such as **7** and **8** and, in particular, at a transition state where steric interactions involving methyl groups are changing, such differences may be significant.

(b) β-Secondary isotope effects, i.e., hyperconjugation,[3c] may play a contributing role, particularly if the reported[35] transition-state polarity is correct. These effects may very well differ depending on CH_3/CD_3 orientation, for instance, in a chair transition state of type **6**. It is perhaps worth emphasizing that discussion of species similar to **5**, as both transition states[35] and intermediate complexes,[31,37] has centered around secondary orbital interactions on the reacting side of the double bond. Hyperconjugative effects of methyl groups on the nonreacting side have been ignored.

(c) Perhaps, most importantly, the natural conformation of DMB is all-perpendicular with alternating up and down C–H bonds parallel to the π-molecular orbital system (cf. ref 38). If interactions of the type depicted in **5** make an important contribution to the product-forming transition state, a 60° rotation of either CH_3 or CD_3 becomes necessary. The enthalpy requirements of such rotations are very significantly different,[38] and the relative dispositions of CH_3 and CD_3 will be critical. In particular, an inverse contribution to k_H/k_D for reaction on the deuterated side of **8** would be anticipated resulting in a *lowering* of the otherwise expected isotope effect. The same would also be true for the intermolecular isotope effect determined for DMB and DMB-$^2H_{12}$ (cf. section 3.3.6.)

We therefore see no need for the assumption of an irreversibly formed complex, with a predestined geometry, as the precursor of product. Indeed, the experimental results in this paper argue strongly against it.

The "product" under discussion could, in the general case, be another transient, in particular, a zwitterion[2] if reaction is carried out in a polar medium. However, we would point out that of those claims of trapping of either open zwitterions[39] or perepoxides,[40] not one set of data appears inconsistent with the interception of an exciplex. Bimolecular reactions of such a species are well-documented,[41] and criticisms that short exciplex lifetimes would

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[32] Wilson, S. L.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 679.

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[34] (a) Baldry, K. W.; Robinson, M. J. T. *Tetrahedron*, **1977**, *33*, 1663. (b) Ellison, S. C. R.; Robinson, M. J. T.; Wright, J. G. *Tetrahedron Lett.* **1985**, *21*, 2585.

[35] Gollnick, K. In ref 36, p 379.

[36] *Oxygen and Oxygen Radicals in Chemistry and Biology*; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981.

[37] Stephenson, L. M. In ref 36, p 371.

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[39] (a) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437. (b) Saito, I.; Matsugo, S.; Matsuura, T. *Ibid.* **1979**, *101*, 7332. (c) Adam, W.; del Fierro, J.; Quiroz, F.; Yang, F. *Ibid.* **1980**, *102*, 2127. (d) Jefford, C. W.; Kohmoto, S.; Boukouvalas, J.; Burger, U. *Ibid.* **1983**, *105*, 6498. (e) Jefford, C. W.; Boukouvalas, J.; Kohmoto, S. *Helv. Chim Acta* **1983**, *66*, 2615. (f) Jefford, C. W.; Jaggi, D.; Boukouvalas, J.; Kohmoto, S. *Ibid.* **1984**, *67*, 1104. (g) Jefford, C. W.; Grant, H. C.; Jaggi, D.; Boukouvalas, J.; Kohmoto, S. *Ibid.* **1984**, *67*, 2210. (h) Saito, I.; Nakagawa, H.; Kuo, Y-H.; Obata, K.; Matsuura, T. *J. Am. Chem. Soc.* **1985**, *107*, 5279. (i) Jefford, C. W.; Boukouvalas, J.; Kohmoto, S. *Tetrahedron* **1985**, *41*, 2081.

[40] (a) Schaap, A. P.; Recher, S. G.; Faler, G. R.; Villasenor, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 1691. (b) Ando, W.; Sonobe, H.; Akasaka, T. *Chem. Lett.* **1987**, 335.

prevent such interception[39d] are ill-founded, particularly where the trapping nucleophile is the solvent.[39a,d,g,i] We would stress that we by no means deny the participation of zwitterionic species in $O_2(^1\Delta_g)$ reaction pathways. We would, however, prefer to adopt an agnostic posture until definitive data are forthcoming. Current time-resolved experiments in these laboratories are concerned with the possibility of characterizing such species spectroscopically.

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Registry No. 1, 57-24-9; **2**, 280-57-9; **3**, 5471-63-6; **4**, 563-79-1; β-C, 7235-40-7; O_2, 7782-44-7; deuterium, 7782-39-0; 2-acetonaphthone, 93-08-3; protoporphyrin IX dimethyl ester, 5522-66-7.

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Formation and Degradation of an Oxalato- and Peroxo-Bridged Dicobalt BISDIEN Dioxygen Complex. Binuclear Complexes as Hosts for the Activation of Two Coordinated Guests

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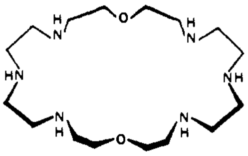
Abstract: The rates of metal-centered degradation of the dioxygen adduct of the binuclear cobalt(II) complexes of 1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane (BISDIEN) have been measured, and first-order rate constants at 60 and 90 °C are reported. The binuclear cobalt(II) complex of BISDIEN, which is intrinsically unstable in solution, is strongly stabilized by coordination of oxalate ion, presumably as a bridging group between the metal centers. Thermodynamic parameters for oxalate binding to protonated forms of the free ligand and to its mono- and dicobalt complex are reported. It has now been found that the dioxygen complex of the dicobalt BISDIEN complex coordinates with and oxidizes a bridging oxalate anion, thus providing the first example of a redox reaction between two coordinated ligands within the cavity of a binuclear macrocyclic complex. Equilibrium data are reported for the formation of the triply bridged (μ-hydroxo, μ-peroxo, μ-oxalato) dicobalt BISDIEN complex, and its concentration has been determined as a function of pH. Rate constants reported for the first-order reaction of dioxygen with oxalate as coordinated entities within the binuclear macrocyclic complex indicate very strong catalysis of oxalate oxidation by molecular oxygen. The reaction proceeds readily at 45 °C, and its rate appears to be largely independent of pH.



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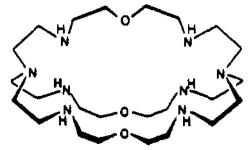

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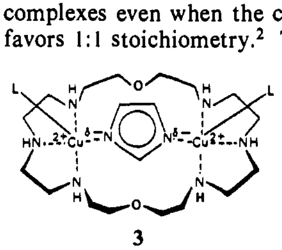

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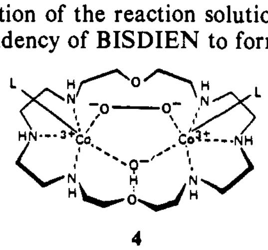

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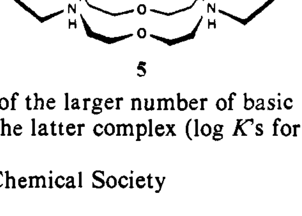
Table I. Equilibrium Constants for the Formation of Dioxygen Complexes of Dicobalt–BISDIEN and Dicobalt–BISTREN Complexes in Aqueous Solution

equilibrium quotient	log K BISDIEN[a]	log K BISTREN[b]
$[HL]/[L][H]$	9.62	9.99
$[H_2L]/[HL][H]$	8.87	9.02
$[H_3L]/[H_2L][H]$	8.28	7.98
$[H_4L]/[H_3L][H]$	7.62	7.20
$[H_5L]/[H_4L][H]$	3.79	6.40
$[H_6L]/[H_5L][H]$	3.31	5.67
$[Co_2L]/[Co]^2[L]$	12.4	16.8
$[Co_2L(O_2)OH][H]/[Co_2L]P_{O_2}$[c]	−3.29	−6.00
$[Co_2L(O_2)(OH)_2][H]/[Co_2L(O_2)OH]$	−8.25	
$[Co_2L(O_2)(OH)_3][H]/[Co_2L(O_2)(OH)_2]$	−9.36	

[a] 0.10 M KCl, 25.0 °C. [b] 0.10 M $NaClO_4$, 25.0 °C. [c] Units are $M{\cdot}atm^{-1}$.



5

It has been found[1] that the binucleating tendency of the macrocyclic hexamine ligand BISDIEN (1,4,10,13,16,22-hexaaza-7,19-dioxacyclotetracosane, BD, **1**) is relatively weak when compared to that of the cryptand O-BISTREN[2] (1,4,10,13,16,22,27,33-octaaza-7,19,30-trioxabicyclo[11.11.11]pentatriacontane, **2**). Because of the flexibility of its macrocyclic ring, BISDIEN forms 1:1 complexes with first-row divalent transition-metal ions in which from four to six nitrogen donors are coordinated to the metal ion. Because of its greater degree of preorganization, O-BISTREN (**2**) tends to form binuclear complexes even when the composition of the reaction solution favors 1:1 stoichiometry.[2] The tendency of BISDIEN to form binuclear complexes is greatly strengthened by combination of its metal complexes with appropriate bridging groups, such as imidazole with Cu(II) to form **3**[1,3] and dioxygen with Co(II) to form the peroxo-bridged complex **4**. The oxygenation constant of the dicobalt(II)–BISDIEN complex is nearly 3 orders of magnitude greater than that of dicobalt(II)–O-BISTREN (**5**; Table I), in spite of the larger number of basic nitrogen donors to cobalt(II) for the latter complex (log *K*'s for oxygenation of

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[1] Motekaitis, R. J.; Martell, A. E.; Lecomte, J. P.; Lehn, J. M. *Inorg. Chem.* **1983**, *22*, 609.

[2] Motekaitis, R. J.; Martell, A. E.; Lehn, J. M.; Watanabe, E. *Inorg. Chem.* **1982**, *21*, 4253.

[3] Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.; Lehn, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 265.

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