of blue copper proteins that are considered fundamental signatures of biological structure and function. The spectral properties of these complexes are influenced strongly by the nature of the thiolate ligand. Substitution in the aromatic ring of benzenethiolate affects the donor properties of the sulfur atom, thereby altering the covalency of the Cu(II)–S interaction. This change in character of the Cu(II)–S(thiolate) bond appears to be the principal cause of perturbations of the Cu(II) site symmetry. These model studies demonstrate that an increase in the covalency of the Cu(II)–S(thiolate) linkage in a pseudotetrahedral $Cu^{II}N_3S$(thiolate) environment can cause the ESR signal to change from one that is qualitatively similar to those of plastocyanin and azurin to one that is qualitatively similar to that of stellacyanin.

The C_{3v} symmetry of the Zn(II) sites in the Zn(II)-R_6 crystal structures[21,22] renders plausible the possibility that a similar geometry may be obtained for some of the Cu(II)-R_6–thiolate derivatives. In view of the spectral similarities that exist between Cu(II)-R_6–PFBT, Cu(II)-R_6–TFBT, azurin, plastocyanin, and the complex tris(pyrazolyl)borate–Cu(II)-2-methyl-2-propanethiolate, we suggest that an approximate C_{3v} geometry is probable for the Cu(II) ion in the Cu(II)-R_6–PFBT and Cu(II)-R_6–TFBT complexes. In contrast, the Cu(II) sites in the Cu(II)-R_6–BT and Cu(II)-R_6-4-MeBT complexes, which give rise to rhombic ESR spectra, appear to be more closely related to the Cu(II) site in stellacyanin, which is predicted[14,30] to possess an effective C_{2v} geometry.

Acknowledgment. We are grateful to the Novo Research Institute (Denmark) for the provision of insulin. We thank Dr. Ole Hvilsted Olsen for providing the computer graphics image of insulin and Professor Guy Dodson for permission to reproduce it. This work was supported by NIH Grant 5-R01-DK 42124-02. The laser Raman instrumentation was purchased with funds from NSF Grant CHE 8805482. ESR analysis software was furnished by the Illinois ESR Research Center, NIH Division of Research Resources, Grant No. RR01811.

Endoperoxide Formation of Helianthrene with Triplet Molecular Oxygen. A Spin-Forbidden Reaction

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Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Frankfurt, Niederurseler Hang, D 6000 Frankfurt/Main, FRG. Received October 28, 1991

Abstract: Dibenzo[*a,o*]perylene (helianthrene = HEL), known to be a very reactive singlet molecular oxygen ($^1O_2$, $^1\Delta_g$) acceptor, also reacts with molecular oxygen in its triplet ground state ($^3O_2$, $^3\Sigma_g^-$) to form helianthrene endoperoxide (HELPO). The thermal endoperoxide formation was studied in several solvents at room temperature. In nonpolar solvents such as toluene and carbon disulfide the temperature-dependent equilibrium, HEL + $^3O_2 \rightleftarrows$ HELPO, is established by the thermolysis of HELPO even at low temperatures. Kinetic parameters for the HELPO formation in toluene are $\Delta H^{*} = 10.2 \pm 1.0$ kcal mol^{-1} and $\Delta S^{*} = -39 \pm 5$ eu, indicating that $^1O_2$ is not involved in the reaction pathway. This is the first example of aromatic endoperoxide formation by reaction with molecular oxygen in its ground state.

Introduction

Helianthrene (HEL) is one of the most reactive $^1O_2$ acceptors known. Measurements of the self-sensitized or methylene blue sensitized photooxygenation have shown that HEL reacts with $^1O_2$ near the diffusion-controlled limit to form the endoperoxide HELPO[1,2] (see Figure 1).

During the investigation of its photooxygenation, it was observed that HEL also reacted with molecular oxygen in the dark. Preliminary tests surprisingly indicated that this dark reaction also led to the formation of HELPO. Such a spin-forbidden reaction between an aromatic compound with a singlet ground state and molecular oxygen in its ground state ($^3O_2$) leading to the endoperoxide with a singlet ground state has—to our knowledge—not previously been observed.[3] We report here a more detailed study of this unique reaction.

Experimental Section

Materials. HEL and 5,7,12,14-tetraphenylpentacene (TP) were synthesized according to literature procedures.[4,5] The solvents used were spectroscopic grade purchased from Aldrich, except for carbon disulfide which was purchased from Merck (Uvasol series). All solvents were purified by column chromatography with neutral Al_2O_3 (Woelm). Tetramethylethylene (TME), 2,6-diphenylisobenzofuran (DPBF), and 2,6-di-*tert*-butyl-4-methylphenol were purchased from Aldrich and used without further purification.

Instruments. Spectroscopic measurements were performed on a Perkin-Elmer 555 or Lambda 5 UV–vis spectrometer. HPLC analyses were done with a Perkin-Elmer 3 B pump using a reversed-phase C_{18} column (Perkin-Elmer) (acetonitrile, Aldrich HPLC grade) and a spectrophotometric UV–vis detector (Perkin-Elmer LC-75) at 290 nm. ESR measurements were performed on a Varian E-12 spectrometer. In all experiments, the starting concentration of HEL was about 1×10^{-4} M, except for in acetonitrile, where its solubility is rather small (max. 5×10^{-5} M). Values for the oxygen concentration in the solvents used[6] are $[O_2] = 2 \times 10^{-3}$ M (air-saturated toluene), 9.5×10^{-3} M (oxygen-saturated toluene), 1.7×10^{-3} M (air-saturated acetonitrile), and 1.1×10^{-3} M (air-saturated iodobenzene).

Solutions with defined concentrations of O_2 were prepared by four pump–freeze–thaw cycles on a vacuum line at 10^{-3} mbar followed by addition of O_2.

In all measurements, extreme care was taken to protect the solutions from light exposure.

Results

1. Thermal Formation of HELPO. Air-saturated solutions of HEL ([HEL] = 8×10^{-5} M) in toluene were allowed to stand for 2 weeks in the dark at 298 K. After this time, the reaction mixture was analyzed with the following results.

1.1. HPLC Analysis. Only two compounds were detected in appreciable amounts (see Figure 2). They could be identified by their retention times as HEL (5.8 min) and HELPO (2.8 min).

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(1) Acs, A.; Schmidt, R.; Brauer, H.-D. *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 1331–1337.

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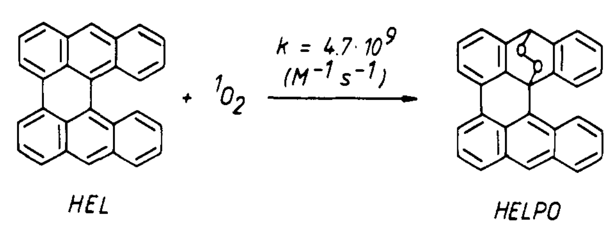


Figure 1.

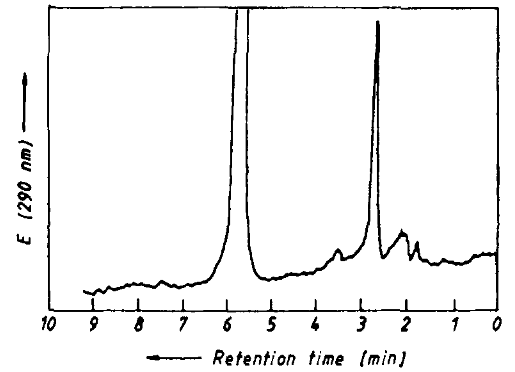


Figure 2. Chromatogram (290 nm) of HEL solution in toluene after standing in the dark at $T = 298$ K for 2 weeks. Retention times: HEL = 5.8 min, HELPO = 2.8 min.

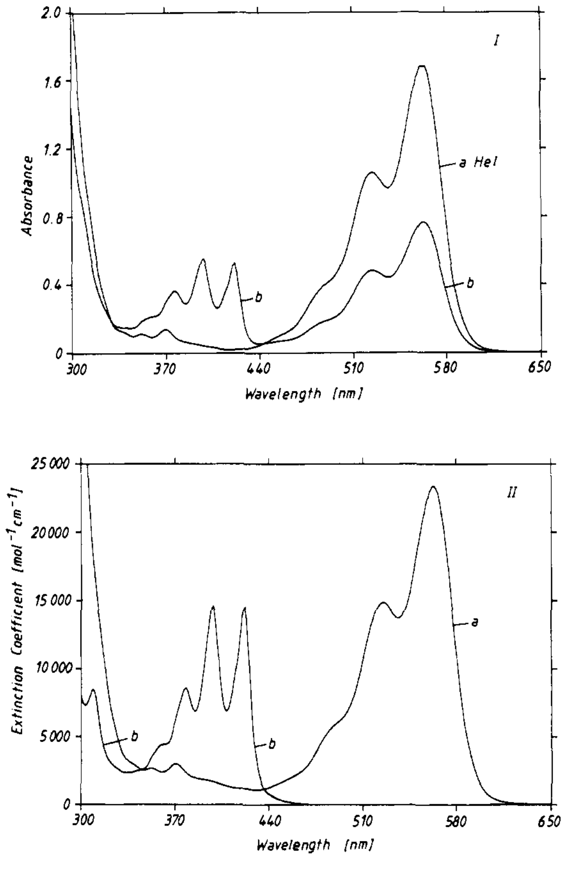


Figure 3. I shows the reaction spectrum of the dark reaction of HEL in air-saturated toluene: (a) spectrum of HEL at $t = 0$; (b) spectrum of the solution after $t \approx 2$ weeks. II shows the reaction spectrum of the self-sensitized photooxygenation of HEL in air-saturated toluene leading to HELPO formation: (a) before irradiation with visible light (HEL spectrum), $\epsilon_{563} = 22\,000$ M^{-1} cm^{-1}; (b) after complete bleaching of the solution (HELPO spectrum).

The addition of photochemically prepared HELPO resulted in no additional peak.

1.2. UV–vis Spectra. The reaction mixture (I in Figure 3, where a = HEL and b = reaction mixture containing HEL and HELPO) exhibits approximately the same spectral properties in the UV region as the spectrum of HELPO (II in Figure 3, where a = HEL and b = HELPO generated by self-sensitized photooxygenation).

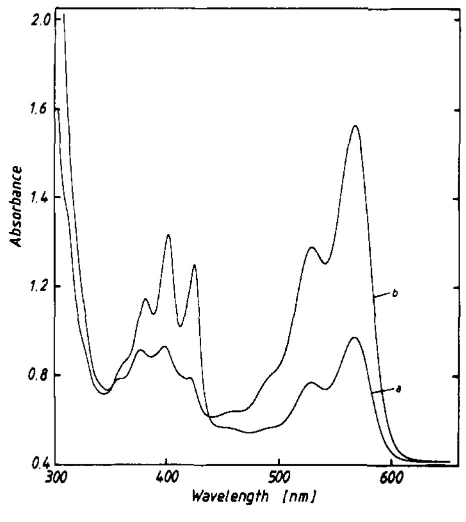


Figure 4. Reaction spectrum of the thermolysis of a toluene solution of thermally generated HELPO: (a) spectrum of an HEL solution in air-saturated toluene after standing in the dark at $T = 298$ K for 2 weeks; (b) spectrum of the same solution after heating for about 3 h at $T = 353$ K.

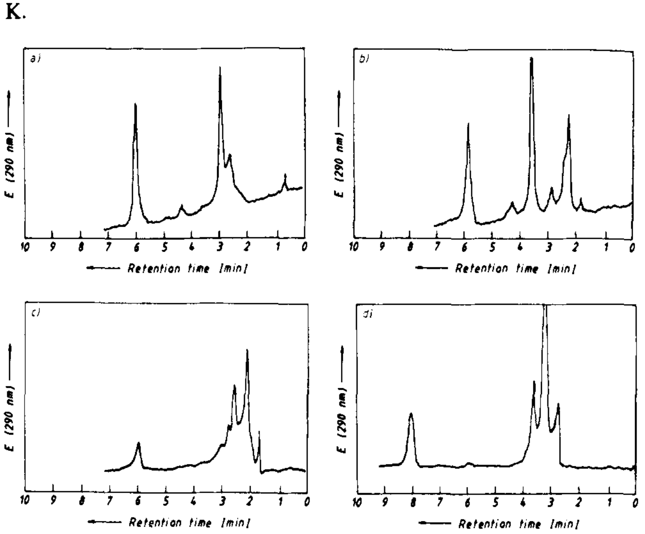


Figure 5. Chromatograms (290 nm) of HEL solutions in different solvents after standing in the dark at $T = 298$ K for 2 weeks: (a) acetonitrile, (b) methanol, (c) dimethylformamide, and (d) dimethyl sulfoxide.

1.3. Thermolysis. Heating a solution of photochemically prepared HELPO in toluene leads to the formation of the parent hydrocarbon HEL. The ability of the thermally generated product to reproduce HEL by thermolysis (as Figure 4 demonstrates) identifies it as HELPO. However, as indicated in Figure 4, heating the reaction mixture does not regenerate HEL exclusively since absorption by an anthracenic chromophore remains. This unidentified compound is probably formed during the thermal oxygenation of HEL, since pure HELPO regenerates HEL completely by thermolysis.

2. Solvent Effect on the Thermal Reaction. HEL was subjected to the thermal reaction with $^3O_2$ in six other air-saturated solvents. The solutions were allowed to stand for 2 weeks in the dark at 298 K and were then analyzed by HPLC. As in the case of toluene (vide supra), solutions in carbon disulfide and iodobenzene formed only traces of byproducts in addition to HEL and HELPO. Except for acetonitrile, where HELPO was still the main product, in all other polar solvents (methanol, dimethylformamide, and dimethyl sulfoxide) HELPO was formed in hardly detectable amounts among many other products (see Figure 5). Therefore, quantitative measurements were performed only with toluene, iodo-

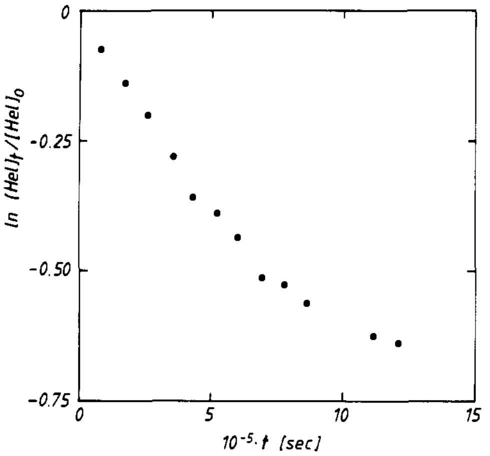
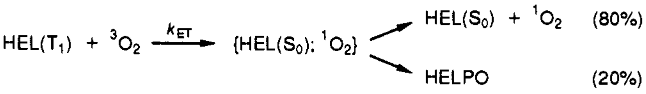


Figure 6. Plot of ln {$[\mathrm{HEL}]_t/[\mathrm{HEL}]_0$} versus t of thermal formation of HELPO in air-saturated toluene at T = 298 K.

Scheme I



benzene, mixtures of both of these, and acetonitrile as solvents.

3. Kinetic Measurements. 3.1. Effect of ${}^1O_2$ Quenchers on the Reaction Rate. To exclude ${}^1O_2$ as a possible intermediate, the thermal oxygenation was performed in air-saturated toluene at 298 K in the presence of an excess of TME as an ${}^1O_2$ trap. As we have shown,[2] in the self-sensitized photooxygenation of HEL, ca. 20% of the HELPO formed resulted from the geminate reaction between HEL in its ground state and ${}^1O_2$ (Scheme I), generated simultaneously by oxygen quenching of the T_1 state of HEL.

In Scheme I, k_{ET} denotes the rate constant of the spin-allowed energy-transfer process. According to Scheme I, one would expect that, if ${}^1O_2$ is involved in the formation of HELPO, 80% of either the thermally or photochemically formed ${}^1O_2$ should be quenched by TME accompanied by a marked decrease in the reaction rate. However, the thermal reaction rate is not influenced by the presence of an about 1000-fold excess of TME ([HEL = 8×10^{-5} M, [TME] = 0.1 M, $k_{TME} = 5 \times 10^7$ M^{-1} s^{-1}),[8] indicating that ${}^1O_2$ is not involved.

3.2. Rate Law of the Thermal Oxygenation of HEL. In air-saturated toluene the thermal oxygenation (eg 1) was studied at 288, 293, 298, and 303 K.

$$\mathrm{HEL} + {}^3\mathrm{O}_2 \xrightleftharpoons[k_{-2}]{k_2} \mathrm{HELPO} \qquad (1)$$

(At temperatures below 288 K, the measurements become very time consuming, and at temperatures above 303 K, the measurements are complicated by the thermal cycloreversion of the product HELPO. Furthermore, the temperature dependence of the oxygen concentrations is not known exactly).

The disappearance of HEL was monitored photometrically at 563 nm and the formation of HELPO at 422 nm. As the plot of ln {$[\mathrm{HEL}]_t/[\mathrm{HEL}]_0$} vs t (Figure 6) demonstrates, even at 298 K the cycloreversion of HELPO cannot be neglected. Since the oxygen concentration in the solution can be regarded as constant under the given conditions ($[O_2] \gg [\mathrm{HEL}]$), the data obey the following integrated rate law:

$$\ln\left[\frac{[\mathrm{HEL}]_t - [\mathrm{HEL}]_e}{[\mathrm{HEL}]_0 - [\mathrm{HEL}]_e}\right] = -(k_2' + k_{-2})t \qquad (2)$$

Here $[\mathrm{HEL}]_0$ and $[\mathrm{HEL}]_t$ denote the concentrations of [HEL] at times $t = 0$ and $t = t$, respectively, $[\mathrm{HEL}]_e$ represents the equilibrium concentration, $k_2' = k_2[O_2]$ is the pseudo-first-order rate constant of forward reaction, and k_{-2} is the first-order rate constant of back reaction of eq 1. $[\mathrm{HEL}]_e$ could not be determined experimentally, since the thermal reaction between HEL and ${}^3O_2$ does not lead exclusively to the formation of HELPO (Figure 1). Thus the kinetic parameters were evaluated by fitting the experimental data to eq 2 using $[\mathrm{HEL}]_e/[\mathrm{HEL}]_0$ as an adjustable parameter, and the $(k_2' + k_{-2})$ values are listed in Table I. At T = 298 K, the thermal oxygenation was also measured in oxygen-saturated toluene to demonstrate experimentally the dependence of k_2' on $[O_2]$ (Table I).

Table I. Kinetic Data of the Equilibrium Reaction (in Toluene)

$$\mathrm{HEL} + {}^3\mathrm{O}_2 \xrightleftharpoons[k_{-2}]{k_2} \mathrm{HELPO}$$

T, K	$[\mathrm{HEL}]_e{}^a$ / $[\mathrm{HEL}]_0$	$10^7(k_2' + k_{-2})$, s^{-1}	$10^7 k_{-2}$,^{b} s^{-1}	$10^4 k_2$,^{c} M^{-1} s^{-1}
288	0.26	7.7 ± 0.4	2.0	2.9
293	0.38	11.7 ± 0.5	4.4	3.7
298	0.47_5	19.4 ± 0.8	9.2	5.1
298	0.47_5	62.4 ± 1.9^d	9.2	5.6^d
303	0.53	33.8 ± 1.4	19.0	7.4

^{a}The values used for the best fit of the experimental data according to eq 2. ^{b}Calculated using the activation parameters for the cycloreversion of HELPO (see text). ^{c}Calculated from $k_2' = k_2[O_2]$ estimated from columns three and four of Table I, assuming that the temperature dependence of $[O_2] = 2 \times 10^{-3}$ M at T = 298 K can be neglected in the range T = 288–303 K. ^{d}Oxygen-saturated solution with $[O_2] = 9.5 \times 10^{-3}$ M.

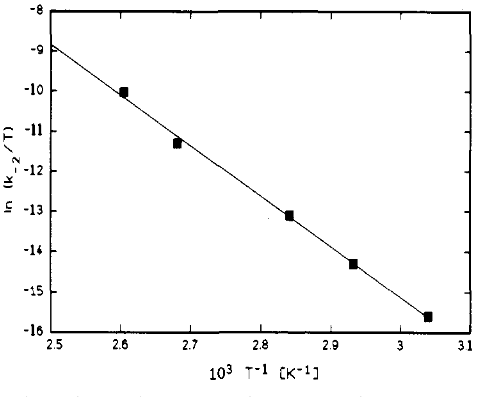


Figure 7. Plot of ln (k_{-2}/T) versus $1/T$ of the cycloreversion of HELPO in N_2-saturated toluene. HELPO was prepared photochemically; $[\mathrm{HELPO}]_0 = 1 \times 10^{-4}$ M.

3.2.1. Cycloreversion of HELPO. For the evaluation of k_2' from $(k_2' + k_{-2})$, values of the rate constant k_{-2} are required at the different temperatures. Therefore we measured the cycloreversion of photochemically prepared HELPO in N_2-purged toluene solutions at five different temperatures from 329 to 384 K. The disappearance of HELPO (the initial HELPO concentration was about 1×10^{-4} M), followed by quantitative HPLC analysis at the 290-nm detection wavelength, demonstrated that HEL was formed quantitatively in a first-order process.

Figure 7 shows the Eyring plot of the k_{-2} values, providing activation parameters of $\Delta H^* = 25.0 \pm 0.8$ kcal mol^{-1} and $\Delta S^* = -2.2 \pm 0.5$ eu. On the basis of these parameters, the rate constants k_{-2} for temperatures in the range 288–303 K were evaluated (see Table I).

To prove that ${}^1O_2$ was not generated by the thermolysis of HELPO, measurements were also conducted in the presence of DPBF and TP, respectively, known to be very reactive ${}^1O_2$ traps. In neither case were oxygenation products of DPBF or TP detected by HPLC (DPBF and TP as well as their oxygenation products proved to be stable under the reaction conditions). Thus ${}^1O_2$ formation by the thermolysis of HELPO cannot exceed an upper error limit of 1%. This is in disagreement with Turro's work on mechanistic investigations of thermolyses of aromatic endoperoxides,[9] according to which HELPO should release mainly ${}^1O_2$

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(7) Wasserman, H. H.; Schaeffer, S. R.; Cooper, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 4991–4996.

(8) Wilkinson, F.; Brummer, J. *J. Phys. Chem. Ref. Data* **1981**, *10*, 836.

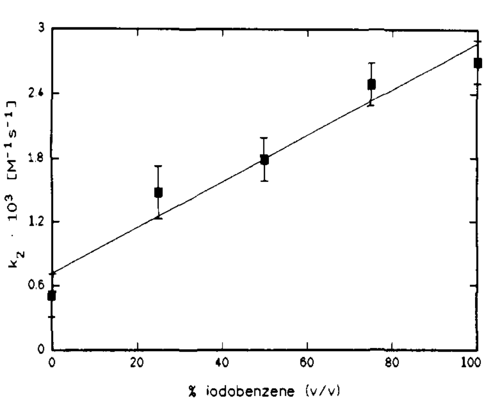


Figure 8. Plot of the rate constant k_2 for the thermal HELPO formation as a function of iodobenzene concentration (v/v) in air-saturated toluene–iodobenzene mixtures (T = 298 K).

by thermolysis since its activation parameters are comparable to those of 1,4-dimethyl-9,10-diphenylanthracene 3,4-endoperoxide, which gives an $^1O_2$ yield of 92% by heating.

3.2.2. Kinetic Data of the Thermal Formation of HELPO. With respect to the pseudo-first-order rate constant k_2', it should be noted that this constant and therefore k_2 too can be evaluated without knowledge of k_{-2}. The constant K of equilibrium 1 is given by the following:

$$K = \frac{k_2'}{k_{-2}} = \frac{[\text{HELPO}]_e}{[\text{HEL}]_e} = \frac{[\text{HEL}]_0 - [\text{HEL}]_e}{[\text{HEL}]_e} \tag{3}$$

Combination of expressions 2 and 3 yields

$$\ln\left[\frac{[\text{HEL}]_t - [\text{HEL}]_e}{[\text{HEL}]_0 - [\text{HEL}]_e}\right] = -\left[\frac{[\text{HEL}]_0}{[\text{HEL}]_0 - [\text{HEL}]_e}\right]k_2't \tag{4}$$

The values of k_2' calculated by eq 4 are in excellent agreement with those estimated from ($k_2' + k_{-2}$) listed in Table I using the k_{-2} values also presented in Table I. The second-order rate constants k_2 for the thermal formation of HELPO estimated from the corresponding k_2' values are listed in Table I. From the Eyring plot of these values, the activation parameters $\Delta H^{\ddagger}$ = 10.2 ± 1.0 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −39 ± 5 eu have been calculated.

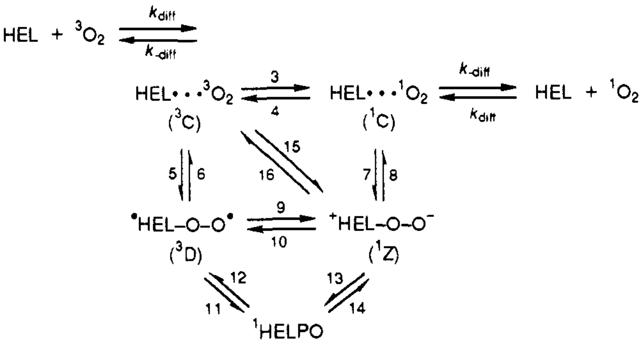
Using the values of k_2' and k_{-2} calculated for the temperature range 288–303 K, the equilibrium constant K for the different temperatures and the standard values for ΔH° and ΔS°, respectively, can be estimated. The value of K decreases from K = 2.85 at 288 K to K = 0.78 at 303 K, resulting in ΔH° = −14.9 ± 2 kcal mol$^-$ and ΔS° = −50 ± 5 eu. Thus HELPO is more stable than HEL on thermodynamic grounds. This can be deduced from structure arguments (see Figure 9).

3.3. Effect of Radical Scavengers on the Reaction Rate. Both the photophysical properties[10] and the results of the self-sensitized or methylene blue sensitized photooxygenation of HEL[1,2] are consistent with a singlet ground state of HEL. This is confirmed by EPR measurements of a degassed toluene solution of HEL ([HEL] = 10^{-4} M) at T = 25 °C which does not exhibit an EPR signal.[11]

To prove that an oxygen biradical like ˙HEL–O–O˙ is not involved in the rate-limiting step of the thermal HELPO formation, 2,6-di-*tert*-butyl-4-methylphenol was added as a radical scavenger, RS ([RS] = 0.1 M; $[\text{HEL}]_0 = 8 \times 10^{-5}$ M). No effect on the reaction rate was observed.

3.4. Solvent Effect. Acetonitrile was the only polar solvent in which the thermal reaction was found to lead predominantly to HELPO. Since the reaction here was not as well-defined as in toluene, we measured only the rate constant at 298 K. For k_2 a value of 1.4×10^{-3} M^{-1} s^{-1} is obtained, which is about a factor of 3 larger than that found in toluene. Although this rate enhancement is relatively modest, it indicates that the thermal formation of HELPO probably occurs via a polar transition state.

Scheme II



3.5. Heavy Atom Effect. A remarkable heavy atom effect on the reaction rate was observed in air-saturated iodobenzene. Figure 8 shows the dependence of the rate constant k_2 on the concentration of iodobenzene in air-saturated toluene solution at 298 K. In going from pure toluene to pure iodobenzene an increase in k_2 by a factor of 5.3 is observed.[12] It is well-established that solvent molecules containing heavy atoms promote intersystem crossing in solute molecules (external heavy atom effect);[13] therefore, the observed enhancement of the reaction rate indicates that spin inversion is involved in the rate-limiting step of the HELPO formation.

Discussion

Turro has considered the sequence in Scheme II for the reaction of an acceptor A with molecular oxygen to produce an oxidized product AO_2, taking into account reactions of A with $^3O_2$ and $^1O_2$, respectively.[14] A = HEL in Scheme II.

Collision of HEL with either $^3O_2$ or $^1O_2$ may yield a loosely bound complex ^{3}C or a complex ^{1}C. Complex ^{3}C may collapse to a diradical ^{3}D, and ^{1}C may collapse to a zwitterion ^{1}Z, both via formation of a single bond from oxygen to HEL (steps 5 and 7). Both intermediates ^{3}D and ^{1}Z may transform directly to the final product HELPO (step 11 or 13) or indirectly via steps 9 and 13 for ^{3}D or 10 and 11 for ^{1}Z, respectively.

On the basis of the results for the photooxygenation of HEL and the thermal oxygenation reported in this paper, one can establish the following facts.

(a) HEL does not quench $^1O_2$ physically as the methylene blue sensitized photooxygenation of HEL has shown.[1,2] Therefore, step 4 in Scheme II can be omitted.

(b) The question of whether the photooxygenation of HEL forming HELPO occurs from ^{1}C in a two-step mechanism via ^{1}Z or via a concerted reaction directly from ^{1}C remains open.

(c) The fact that addition of a large excess of TME to the reaction solution does not inhibit the thermal formation of HELPO indicates that $^1O_2$ is not involved in the reaction pathway and eliminates step 3 in Scheme II. This conclusion is supported by the value of $\Delta H^{\ddagger}$ = 10.2 kcal mol^{-1} determined for the thermal HELPO formation in toluene, which is less than half the energy required to produce $^1O_2$ in a spin-forbidden process.

(d) The formation of a long-lived biradical ^{3}D can be excluded, since the rate of thermal HELPO formation in the presence of a radical scavenger is not affected.

(e) The higher value of k_2 found in acetonitrile compared to that found in toluene indicates that the reaction probably occurs via a polar transition state. The acceleration of the thermal HELPO formation by iodobenzene shows that additionally a spin

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(9) Turro, N. J.; Ming Fea Chow; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218–7224.

(10) Friedrich, K. A. Diplomarbeit, University of Frankfurt, Frankfurt/Main, FRG, 1987.

(11) A referee has suggested that HEL could be a ground-state biradical.

(12) The oxygen concentrations of the iodobenzene–toluene mixtures were calculated on the following assumption:

$$[O_2]_{mix} = [O_2]_T\text{vol\%(T)} + [O_2]_I\text{vol\%(I)}$$

in which $[O_2]_{mix}$ is the total concentration in the mixture and $[O_2]_T$ and $[O_2]_I$ are the concentrations in pure toluene and iodobenzene, respectively.

(13) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; pp 209–211.

(14) Turro, N. J. *Tetrahedron* **1985**, *41*, 2089–2098.

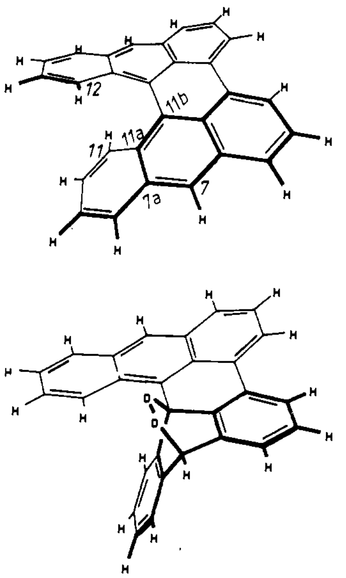

Figure 9. Structures of HEL and HELPO computed with the molecular mechanics package of Gajewski and Gilbert.[15]

Scheme III

$$\mathrm{HEL} + {}^3\mathrm{O}_2 \underset{k_{-\mathrm{diff}}}{\overset{k_{\mathrm{diff}}}{\rightleftharpoons}}$$

$$\underset{({}^3\mathrm{C})}{\mathrm{HEL}\cdot\cdot\cdot{}^3\mathrm{O}_2} \underset{k_{16}}{\overset{k_{15}}{\rightleftharpoons}} \underset{({}^1\mathrm{Z})}{{}^+\mathrm{HEL{-}O{-}O}^-} \underset{k_{14}}{\overset{k_{13}}{\rightleftharpoons}} \mathrm{HELPO}$$

inversion is involved in the rate-limiting step. Therefore, the most probable pathway for the thermal formation of HELPO with respect to Scheme II is via ^{3}C directly to ^{1}Z. The assumption of the formation of a zwitterion is consistent with the observation that the reaction of HEL with $^3O_2$ in polar solvents leads mainly to products other than HELPO. We assume that the involved zwitterion is subject to side reactions and rearrangement caused by the nucleophilic attack of solvent molecules. The fact that thermolysis of photochemically prepared HELPO in methanol yields HEL only in a minor amount among many byproducts confirms this assumption.

Therefore, we postulate that the loosely bound complex ^{3}C formed by collision of HEL and $^3O_2$ reacts directly in a spin-forbidden step (step 15) under charge transfer from HEL to oxygen to ^{1}Z, transforming into HELPO (step 13), as illustrated in Scheme III.

A possible explanation for this unique behavior of HEL to yield an endoperoxide by reaction with triplet oxygen is based mostly on its special structure (Figure 9).[15] As shown for the first time by Theilacker and Thomas,[16] HEL and its derivatives cannot be planar in spite of the fact that all of their carbon atoms are sp^2-hybridized. The hydrogens at carbon atoms 11 and 12 cause a steric hindrance which forces the two benzo rings to twist out of the plane of the aromatic system. Accordingly, HEL is asymmetrical and appears in two enantiomers.[16] The twist of the two external benzo rings probably introduces a strong strain in the double bonds at carbons 7/7a and 11a/11b, which may provide the energy required for the reaction. In the endoperoxide this strain is absent, which is evident from the structure of HELPO depicted in Figure 9. This accounts not only for the ability of HEL to accept $^3O_2$ but also for its very high reactivity toward $^1O_2$.

Acknowledgment. We thank the Fonds der Chemischen Industrie for their financial support.

Registry No. HEL, 190-36-3; HELPO, 25305-13-9.

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[15] The structures were computed with the molecular mechanics package by S. S. Gajewski and K. E. Gilbert, Serena Software, Box 3076 Bloomington, IN 47402.

[16] Theilacker, W.; Thomas, W. *Liebigs Ann. Chem.* **1960**, *632*, 115–117.