possible to suppress fingering by increasing the nitric acid concentration because R_ρ' will asymptotically approach R_ρ, which is unity and optimal for finger formation.[19] The difference between the descending velocity and the reaction-diffusion velocity should approach a constant value at higher acid concentrations. Unfortunately, this could not be confirmed because the solutions were not stable at high acid concentrations.

In the chlorite-thiosulfate system, the descending fronts were the fastest at low concentrations, while at higher concentrations the reverse behavior occurred.[11] How can this be, given that the stability ratio is independent of concentration? The chlorite-thiosulfate system is not adiabatic and is profoundly affected by the medium that surrounds the tube. The stability ratio, R_ρ, is approximately 8, based on a $\Delta\rho_c$ of 2×10^{-4} g/cm^3 for $[ClO_2^-]_0 = 0.03$ M.[11] At low concentrations, $R_\rho' < 8$ and fingers form. At high concentrations, R_ρ' is closer to R_ρ. A stability ratio of 8 is apparently sufficient to suppress fingering. This contrasts with the finding of Huppert and Manins[19] that the critical R_ρ must exceed 700. However, their work was based on an analogy with the sugar-salt system and much larger density differences.

Conclusion

Because there is an isothermal increase in density, $\Delta\rho_c$, which compensates for the thermally induced density decrease caused by the heat released during the reaction, simple convection is not expected to occur in the iron(II)-nitric acid system. However, because the two factors affecting the density have different transport coefficients, "double-diffusive" or multicomponent convection may take place.

Ascending fronts produce a solution configuration that corresponds to the "diffusive" regime in which the hot, salty water lies under cool, fresh water. Convection can increase the effective mass transport coefficient by as much as 10 times, resulting in an increase in propagation velocity of a factor of 3. The front remains sharp with convection occurring above it.

Descending fronts produce a solution configuration that corresponds to the "fingering" regime in which hot, salty water lies over cool, fresh water. "Salt fingers" occur which increase the effective mass transport coefficient by as much as 5 orders of magnitude. Front velocities can be increased by as much 100 times, depending on the width of the tube.

In order to obtain a quantitative model of the experiments, more work must be done on the theory of multicomponent convection. Perhaps results from experiments on chemical waves may also assist in understanding multicomponent convection in narrow tubes.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8800169) and by a U.S.-Hungarian cooperative grant from the NSF and the Hungarian Academy of Sciences. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Kenneth Kustin and István Lengyel for their critical readings of the manuscript.

Rate Parameters for the Two-Step Photofragmentation of Aromatic Endoperoxides in Solution

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The formation of dimethylhomöocoerdianthrone (HOCD) following subpicosecond laser photolysis of its endoperoxide (PO) was studied by laser-induced fluorescence (LIF) in the solvents dichloromethane and toluene. The measured rise time of the LIF signal refers to a time constant of $\tau_2 = 1.7 \pm 0.5$ ps at 22 °C. The study of the characteristic rate constant at different temperatures gives an activation energy of $E_a = 5.5 \pm 0.5$ kcal/mol and a preexponential factor of $A = 10^{15.7\pm0.3}$ s^{-1} in toluene. These parameters are consistent with our earlier model for the two-step photofragmentation of aromatic endoperoxides, which assumes a short-lived 1,6-biradical intermediate crossing an activation barrier. The photolysis study of the newly synthesized endoperoxide of anthrabisbenzothiopyran (ABTPO) reveals that photocycloreversion starting from $S_3(\pi\pi^*)$ proceeds with a time constant of $\tau_2 = 46 \pm 6$ ps in dichloromethane (at 22 °C). In this case the activation parameters amount to $E_a = 5.9 \pm 0.6$ kcal/mol and $A = 10^{14.8\pm0.3}$ s^{-1}. The observed activation barrier on the potential energy surface can be a result from resonance effects in the chromophores of the peroxy biradical. The large A factors reflect the importance of internal degrees of freedom in the transition state.

Introduction

To obtain extensive information about the intramolecular transfer of excitation energy in condensed molecules, steady-state and time-resolved investigations of the photochemistry of aromatic endoperoxides (POs) have been performed in the last decade. On the basis of orbital and state correlation diagrams, Kearns and Khan[1,2] expected that the photofragmentation of POs starts in contrast to the commenly accepted rule of Kasha,[3] from upper excited $(\pi_{cc}\sigma_{co})$ singlet states $S_{n\geq2}$, reproducing the parent hydrocarbon in S_0 and singlet oxygen $(^1\Sigma_g^+)$. The photochemical reaction path was characterized to be concerted and adiabatic and is denoted "photocycloreversion". Another route envisaged takes place from $S_1(\pi^*\sigma^*)$, leading exclusively to the homolytic rupture of the peroxide bridge, followed by recombination or irreversible rearrangement. The reverse reaction path corresponds to the sensitized photooxygenation of the aromatic compound.

Numerous steady-state investigations on the wavelength dependence of the photochemistry of POs have confirmed these predictions meanwhile.[4-8] However, two important questions

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(1) Kearns, D. R.; Khan, A. U. *Photochem. Photobiol.* **1969**, *10*, 193.
(2) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *19*, 6554.
(3) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14.
(4) Schmidt, R.; Drews, W.; Brauer, H.-D. *J. Am. Chem. Soc.* **1980**, *102*, 2791.
(5) Drews, W.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1980**, *70*, 84.
(6) Drews, W. Dissertation, University of Frankfurt am Main, 1980, FRG.

TABLE I: Time Constants τ_2 and Quantum Efficiencies Q_c for the Photocycloreversion of Aromatic Endoperoxides (at 22 °C)

PO	τ_2, ps	Q_c
HOCDPO[a]	2 ± 2 (1.6 ± 0.5[b])	0.52
HECDPO[a]	40 ± 10	0.27
ADCPO[a]	55 ± 15	0.13
BDXPO[a]	68 ± 8	0.18
9,10-DMDPO[4]c	75 ± 20	0.31
1,4-DMDPO[c]	50 ± 15	0.8
9,10-DPAPO[d]	95 ± 10	0.28
9,10-PAPO[e]	60 ± 7	0.28

[a] Reference 11–13. [b] Reference 14. [c] POs of 1,4-dimethyl-9,10-diphenylanthracene.[8] [d] PO of 9,10-diphenylanthracene.[10] [e] PO of 9-phenylanthracene.[10]

concerning the mechanism of photocycloreversion arise: (a) The existence of the presumed product $O_2(^1\Sigma_g^+)$ cannot be verified presently in experiments, because its radiationless deactivation to $O_2(^1\Delta_g)$ occurs too fast in solution. Thus, the precise state of the primary product $^1O_2$ remains an open question. (b) For a series of endoperoxides a 1:1 correlation in the formation of the anthracene fragment (A) and $^1O_2$ was observed.[5] In the first instance one tends to adopt the concept of a concerted one-step mechanism, which consists of breaking both C–O bonds simultaneously. Nevertheless, this assumption can be verified solely by information about the time evolution of photocycloreversion, for the rise time of photofragments (A + $^1O_2$) has to be equal to the lifetime of the excited singlet state in the concerted case.

The question of concerted mechanism was tackled by us recently in using picosecond pulsed light sources to study the photocycloreversion of the PO of heterocoerdianthrone (HECD).[9] From the rather slow time evolution of hydrocarbon (40 ps) and the short-lived excited $S_3(\pi\pi^*)$ state (<3 ps) followed, in contrast to Kearns' prediction, that photocycloreversion must proceed via an intermediate. The time constants for decay of the intermediate yielding A and $^1O_2$ are found to range between 1.6 and 95 ps depending on PO (see Table I). The quantum efficiency of this process (Q_c) is limited only by a deactivation path leading from the $\pi\pi^*$ state via internal conversion to S_1 and amounts for some POs up to 80%.[5,8] In light of the fact that the kinetics of photocycloreversion is not influenced by the polarity or viscosity of solvent, we favor the model of sequential C–O bond rupture via a biradical intermediate.[11] A temperature-dependent study of the dynamics of the photocycloreversion of HECDPO exhibits that the decay of intermediate yielding HECD (S_0) and $^1O_2$ is activation controlled.[12]

The fastest kinetics for the photocycloreversion of an aromatic PO was observed by us[13] and independently by Ernsting et al.[14] in the case of dimethylhomöocoerdinanthrone endoperoxide (HOCDPO). This compound can be treated as an isomer of HECDPO having two additional methyl groups. In our past photolysis study of HOCDPO we have measured a time constant of τ_2 = 2 ± 2 ps for the rate-determining step of photocycloreversion, which is comparable to the response time of the picosecond apparatus (τ_{app} = 2.5 ps). Using subpicosecond transient absorption techniques, Ernsting found briefly that HOCD formation following photolysis of its PO happens with a time constant of τ_2 = 1.6 ± 0.5 ps. The motivation of this work lies now in providing comprehensive information on the striking dynamics observed in the case of HOCDPO decomposition. Therefore, a subpicosecond light source was developed, and laser-induced fluorescence (LIF) was applied as detection tool. The photocycloreversion of HOCDPO was studied in two solvents and at different temperatures. The rate parameters are presented in Arrhenius' and Eyring's formulation.

A newly synthesized endoperoxide with similar chromophore structure is anthrabisbenzothiopyran endoperoxide (ABTPO). The results from a photolysis study on ABTPO support further the outlined biradical model.

Experimental Section

The picosecond laser system has been characterized recently.[13] For direct observation of the dynamics of photocycloreversion, the method of pump–probe interrogation is used, probing the aromatic moiety with LIF. The picosecond pulses are generated in a hybridly mode-locked dye laser (Model Coherent 702.1 CD; 2 ps fwhm, 10 nJ) working with rhodamine 6G as gain medium and DODCI as saturable absorber. The pulse energy can be increased up to 0.3 mJ in a three-stage dye amplifier (Model Lambda Physik FL2003), which is pumped by a XeCl laser at 1-Hz repetition rate. After frequency doubling in a KDP crystal with 10% efficiency of UV light, the pulses are split into the second and first harmonic by means of a dichroic mirror. The visible pulses travel eventually a variable delay line and are focused collinearly with the UV pulses into the sample cell. The response time of the apparatus (τ_{app} = 2.5 ps) was determined by observing the stimulated S_1 emission from bleached rhodamine B molecules.[15]

To investigate the photochemistry of HOCDPO, we optimized the time resolution of the picosecond laser system in compressing the visible pulses by addition of malachite green to the saturable absorber and by using a compressor stage.

The additional mixing of malachite green ($c \approx 2 \times 10^{-6}$ M) to the absorber dye DQOCI shortens the pulses by a factor of about 7 due to the optical properties of malachite green, such as an ultrafast absorption recovery time of 2.1 ps and a large absorption cross section.[16] Thereby pulses with a duration of 320-fs fwhm and an energy of 7 nJ are generated. The central wavelength λ_L of the laser pulses is slightly blue shifted by malachite green (≈4 nm) and can be tuned in the range 570–590 nm with the help of a Lyot filter ($\Delta\lambda \approx$ 1 nm).

Further pulse compression is acquired in coupling the 320-fs pulses into 80 cm of polarization-preserving, single-mode optical fiber (Newport Research Corporation F-SPV) with 60% coupling efficiency. Self-phase modulation and the group velocity dispersion act together and broaden the pulses both spectrally and temporally. Finally, the recollimated pulses are compressed by passage through a dispersive delay line consisting of two 1200 line/mm holographic diffraction gratings (separation of 10 cm, 70% diffraction efficiency). The resulting pulses have a width of about 100-fs fwhm and an overall energy of 1.5 nJ, being insufficient for studying state-selective photochemistry. Therefore, we start in our experiments with 320-fs pulses having an energy of 7 nJ. Amplification of these pulses in the three-stage dye amplifier FL2003 increases the energy to 0.15 mJ and the high peak power to 450 mW. The response time of the subpicosecond laser system is determined as pointed out above and amounts to τ_{app} = 0.8 ps. The apparatus function $A(t)$ has to be taken into account when fitting the experimental data by a single-exponential rise term $\int A(t)[1 - \exp(-t/\tau_2)]\,dt$.

The procedure of temperature variation is described in ref 12. HOCDPO was prepared and purified following earlier published procedures.[17] The synthesis of ABTPO is described in ref 18.

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(7) Brauer, H.-D.; Schmidt, R. *Photochem. Photobiol.* **1985**, *41*, 119.

(8) Eisenthal, K. B.; Turro, N. J.; Dupuy, C. G.; Hrovat, D. A.; Langan, J.; Jenny, T.; Sitzmann, E. V. *J. Phys. Chem.* **1986**, *90*, 5168.

(9) Blumenstock, T.; Comes, F. J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1986**, *127*, 452.

(10) Sitzmann, E. V.; Langan, J. G.; Hrovat, D. A.; Eisenthal, K. B. *Chem. Phys. Lett.* **1989**, *162*, 157.

(11) Blumenstock, T.; Jesse, K.; Comes, F. J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys.* **1989**, *130*, 289.

(12) Jesse, K.; Comes, F. J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1989**, *160*, 8.

(13) Jesse, K.; Markert, R.; Comes, F. J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1990**, *166*, 95.

(14) Ernsting, N.; Schmidt, R.; Brauer, H.-D. *J. Phys. Chem.* **1990**, *94*, 5252.

(15) Shank, C. V.; Ippen, E. P.; Teschke, O. *Chem. Phys. Lett.* **1977**, *45*, 291.

(16) Watanabe, A.; Takemura, H.; Tanaka, S.; Kobayashi, H.; Hara, M. *IEEE J. Quant. Electron.* **1983**, *QE-19*, 533.

(17) Schmidt, R.; Drews, W.; Brauer, H.-D. *Z. Naturforsch* **1982**, *37a*, 551.

(18) Schaffner, K. Dissertation, University of Frankfurt am Main, 1989, FRG.

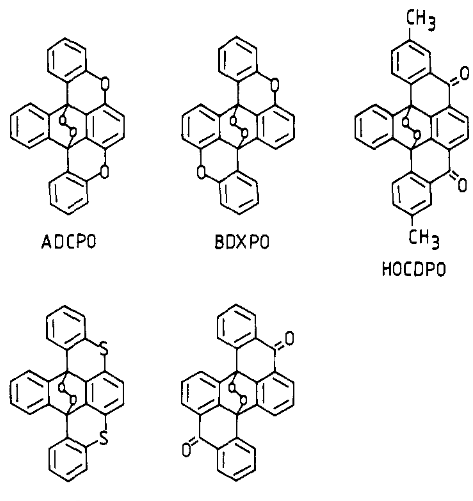

Figure 1. Structure formulas of some 9,10-endoperoxides from the anthracene series (HECD = heterocoerdianthrone, HOCD = dimethylhomöocoerdianthrone, ADC = anthradichromene, BDX = benzodixanthene, ABT = anthrabisbenzothiopyrane).

TABLE II: Energetics of the Photocycloreversion of Some 9,10-Endoperoxides with $^1O_2(\Delta_g)$ as Primary Product

PO	$S_n(\pi\pi^*)$	E, cm^{-1}	ΔH, cm^{-1}
HOCDPO	S_3	28 500	17 000
HECDPO	S_3	31 800	19 700
ADCPO	S_2	32 000	21 700
BDXPO	S_2	31 800	21 500
ABTPO	S_2	28 000	not given
	S_3	31 000	not given
	S_5	40 000	not given

As solvents we used dichloromethane and toluene from the Uvasol series of Merck.

Results

The structural formulas of the investigated 9,10-endoperoxides from the anthracene series are shown in Figure 1. In comparison with the POs studied by Eisenthal et al.[8,10] the phenyl substituents of our POs are connected with the anthracene frame by carbonyl, ether, or sulfur bridges in the 1,4 or 1,5 position. Consequently this causes a rigid conformation of PO and leads to an enormous red shift in absorption of the aromatic compound due to conjugation effects.

Upon excitation into $S_n(\pi\pi^*)$ states of the aromatic chromophores, POs undergo cycloreversion to form the anthracene moiety and singlet oxygen. The energetic location of these singlet states (E) and the exothermicity of photocycloreversion (ΔH) are listed in Table II. While the energetics of the singlet photochemistry is taken from the electronic spectra of POs, the excess energy of products (A + $^1O_2(\Delta_g)$) is estimated on the basis of Hess's theorem. We can calculate ΔH easily as the difference $E - (\Delta H_T - \Delta H_P^{\ddagger})$, where E is the excitation energy and $\Delta H_T^{\ddagger}$, $\Delta H_p^{\ddagger}$ are the enthalpics of activation of thermolysis and photooxidation.[4] The latter process occurs with almost zero activation enthalpy ($\Delta H_p^{\ddagger} \approx 0$).[19]

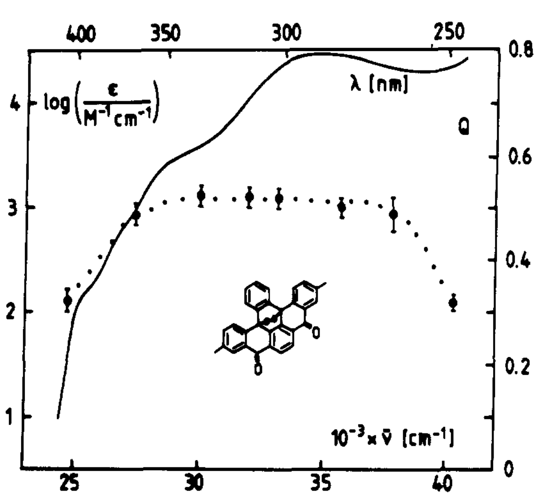

Figure 2. Absorption spectrum of HOCDPO and the quantum efficiency of photocycloreversion (Q_c); the solvent is dichloromethane.[7]

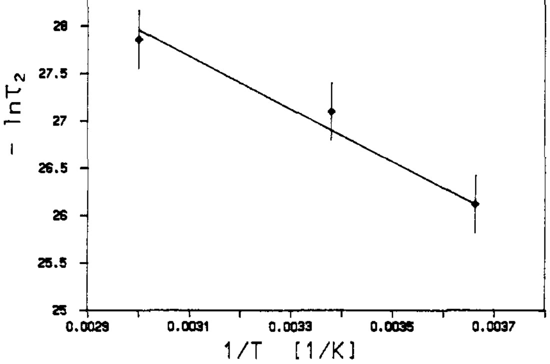

Figure 3. Arrhenius plot of the rise time τ_2 of HOCD from photolysis of its PO; the solvent is toluene: slope = −2780 K; intercept = 36.3; correlation = 0.985.

TABLE III: Rate Parameters for the Photocycloreversion of Some Aromatic Endoperoxides (at 22 °C)

PO	solvent	A, s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal
HOCDPO	toluene	$10^{15.7}$	5.5	≈11	4.9
HECDPO	toluene	$10^{14.8}$	5.7	≈7	5.1
	chlorobenzene	$10^{14.4}$	5.3	≈7	4.7
ABTPO	CH_2Cl_2	$10^{14.7}$	5.9	≈7	5.3

The absorption spectrum and the wavelength dependence of Q_c are illustrated for HOCDPO in Figure 2; the solvent is dichloromethane. It is obvious that Q_c does not change significantly in the region 260–370 nm, where the $S_3(\pi\pi^*)$ and $S_4(\pi\pi^*)$ bands overlap. Hence, Brauer et al. conclude that the deactivation of the S_4 state to S_3 occurs completely nonradiatively via internal conversion (IC).[6] In our past study on the photochemistry of POs we could demonstate the IC between the upper excited singlet states must proceed at least 1 order of magnitude faster than the observed second step in photocycloreversion.[13] This behavior can also be expected on the basis of the energy gas rule for radiationless transitions.[20] The experimentally observed reaction pathway of HOCDPO thus consists of an excitation of the PO with a femtosecond pulse at 293 nm to the $S_4(\pi\pi^*)$ state, which decays via IC to $S_3(\pi\pi^*)$ from which photocycloreversion proceeds. The formation of HOCD is monitored by LIF using a weak probe pulse at 586 nm with variable time delays. The probe wavelength lies close to the absorption maximum of HOCD in order to avoid temperature effects on the red wavelength onset of the S_1 band that may result from the large excess energy of 17 000 cm^{-1}.

The rise of LIF signal refers to a time constant of τ_2 = 1.7 ± 0.5 ps (at 22 °C) in the two solvents dichloromethane and toluene and confirms the result obtained by Ernsting et al.[14] The temperature dependence of the rate constant is depicted by an Arrhenius plot in Figure 3. Apparently, τ_2 decreases from 4.5 to 0.8 ps when the temperature is increased from 0 to 60 °C. An activation energy of E_a = 5.5 ± 0.6 kcal/mol and a preexponential factor of $A = 10^{15.7\pm0.3}$ s^{-1} can be calculated from the slope and intercept of the drawn straight line, which is a result of a regression analysis. The A factor for the photofragmentation of HOCDPO

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(19) Seikel, K. Dissertation, University of Frankfurt am Main, 1990, FRG.

(20) Turro, N. J. *Modern molecular photochemistry*; Benjamin Cumming: Menlo Park, CA, 1978; p 182.

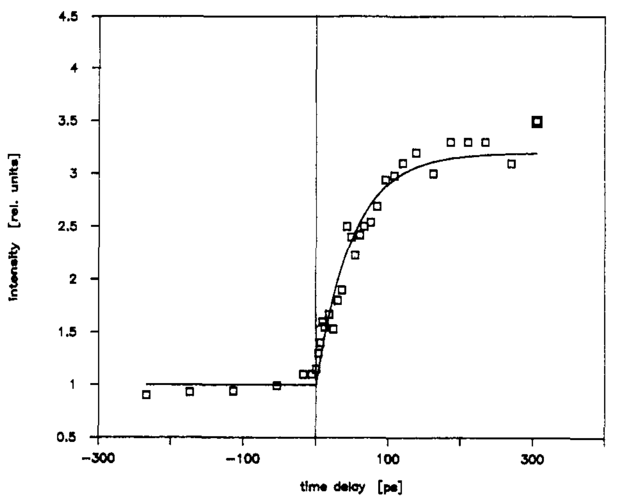

Figure 4. Rise of LIF signal from photodecomposition of ABTPO refers to a time constant of 46 ± 6 ps in dichloromethane (at 22 °C).

is about 1 order of magnitude larger than in the case of HECDPO, whereas the activation energies are similar (see Table III).

From a comparison of the molecular structure of the two endoperoxides ADCPO and ABTPO, it is evident that the only difference originates from the replacement of ether by sulfur bridges. But in contrast to ADCPO, photocycloreversion of ABTPO starts from several ($\pi\pi^*$) singlet states (S_2, S_3, S_5).[21] To get time information about this process, we pumped the molecule with a pulse at 288 nm to the S_4 state, which relaxes completely via rapid IC to $S_3(\pi\pi^*)$. With a second pulse of 576 nm we probed for ABT formation ($Q_c = 0.04$). In this way we measured a LIF rise time of $\tau_2 = 46 \pm 6$ ps (see Figure 4), exhibiting the same temporal behavior as observed in the photolysis study of ADCPO. Kinetic data about the thermal stability of ABTPO(S_0) were not available, so that we had to confine ourselves in our temperature-dependent study of τ_2 to temperatures below 20 °C. From this study results an activation energy of $E_a = 5.9 \pm 0.5$ kcal/mol and a preexponential factor of $A = 10^{14.7\pm0.3}$ s^{-1}, respectively.

Discussion

The adiabatic photocycloreversion of POs producing the aromatic hydrocarbon and $^1O_2$ occurs in two steps and takes 1–100 ps for the investigated compounds. The fact that the hydrocarbon rise times, τ_2, are not influenced by polarity or viscosity gives strong evidence that the short-lived intermediate has biradicaloid structure. In our preliminary discussion we have classified this intermediate as a 1,6-biradical, which is formed by the cleavage of one C–O bond in the PO molecule. In this connection we should mention that Eisenthal et al. pointed out a possible second reaction pathway, involving rapid expulsion of $^1O_2$ from the excited-state endoperoxide and leaving an excited valence anthracene isomer with substantial biradical character.[10] The two possibilities of the biradical model are elucidated schematically in Figure 5.

To evalute these two mechanisms, we must have a look at the enthalpies of formation for the 1,6-peroxy aromatic and the 1,4-aromatic type biradical. For the purpose of simplicity we will consider only the anthracene frame in our calculations. For the estimation of enthalpies of formation we have used tabulated values of bond enthalpies.[22] No doubt such an extimation has an uncertainty of at least 10%. Following these arguments we are led to the conclusion that the formation of the 1,6-peroxy biradical from anthracene endoperoxide requires an energy of $\approx$29 000 cm^{-1}, whereas the 1,4 valence isomer can be formed by raising an energy amount of $\approx$40 000 cm^{-1}. If one now compares these enthalpies with the energetics of photocycloreversion (Table II), it seems clear that the second reaction pathway proposed by Eisenthal et al. has to be ruled out. Consequently, if a biradical is the intermediate in the two-step photofragmentation of POs, it is the 1,6 biradical (BR).

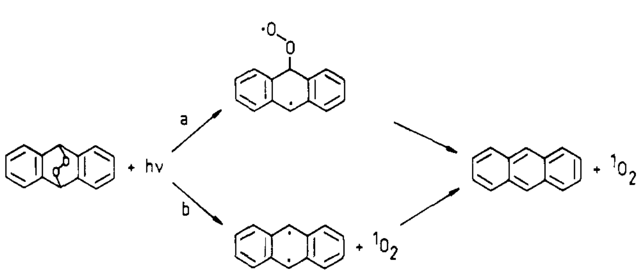

Figure 5. Biradical mechanism for photocycloreversion of aromatic endoperoxides provides two pathways: (a) the sequential C–O bond breaking to form a 1,6 biradical or (b) the homolytic rupture of both C–O bonds to produce singlet oxygen and an aromatic valence isomer.

The first step of photocycloreversion to form BR is expected to occur very rapidly. Beswick and Jortner characterized direct dissociation dynamics by two distinct time scales.[23] A time scale of $\sim 10^{-14}$–10^{-15} s is assumed for the dephasing of the initial nuclear wavepacket on the dissociative potential surface and respectively a time scale of $\sim 10^{-13}$ s for bond rupture, which is typically a vibrational period.

The investigated 9,10-endoperoxides (except HOCDPO) decompose from the excited ($\pi\pi^*$) state on a time scale of about 50 ps, which is an extension of 2 orders of magnitude with respect to BR formation and must be related therefore to the lifetime of BR. Now, the essential and difficult question arises as to what parameters determine the biradical lifetimes. In principle, various mechanisms can be responsible to control the decay of a biradical intermediate in unimolecular reactions. For instance, intersystem crossing (ISC) is known to determine the biradical lifetime in many cases. The rate of intersystem crossing depends on the distance between radical centers and orbital orientation (Salem's rule).[24] However, the short time scale of photocycloreversion and the 1:1 formation of products in singlet states are actually against the idea of an ISC-controlled decomposition.

Moreover, the possibility of a biradical recombination to yield ground-state PO has to be thought over in analogy to the radiationless deactivation of PO(S_1) molecules, which occurs chemically via homolytic O–O bond rupture and subsequent O–O bond reformation.[4] However, this idea is out of the question, because τ_2 depends on temperature, but not Q_c.[12] Therefore τ_2 must be related to the reaction BR → A + $^1O_2$.

In the following we try to find a kinetic access to the understanding of the outlined biradical model. The adiabatic photofragmentation of aromatic POs occurs via sequential C–O bond rupture. The rate parameters that are obtained from a temperature-dependent study of the rate-determining constant indicate that a barrier such as 5–6 kcal/mol appears on the excited PES. It is common knowledge in radical chemistry[25] that π-conjugated biradicals have much longer lifetimes than other biradicals due to conjugation between the radical centers and an increased singlet–triplet gap. Examples for resonance-stabilized radicals are the biradicals of naphthoquinodimethane having lifetimes between 200 ps and 150 s.[26-28] Thus, it is most likely that the rather high activation barrier found for BR decomposition reflects the importance of resonance interactions associated with the radical center and the π electronic systems of the 9,10-phenyl substituents. Eisenthal et al. interpreted the observed long BR lifetimes for unbridged POs in terms of structural effects.[10] We demonstrated in a former paper on this topic that the crossing of the barrier

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(21) Schaffner, K.; Brauer, H.-D., to be published.

(22) Pauling, L. *The nature of the chemical bond and the structure of molecules and crystals. An introduction to modern structural chemistry*; Cornell University Press: Ithaca, NY; 1939; Chapter XIV.

(23) Beswick, J. A.; Jortner, J. *Chem. Phys. Lett.* **1990**, *168*, 246.

(24) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(25) Viehe, H. G., Janousek, A., Merenyi, R., Eds. *Substituent effects in radical chemistry*; NATO ASI Series; Reidel: Dordrecht, 1986; Series C, Vol. 189.

(26) Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1192.

(27) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

(28) Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 583.

J. Phys. Chem. **1991,** *95,* 1315-1318 **1315**

is a solvent-independent and thermally activated process.[12]

A first attempt to interprete the large preexponential factors (10^{15-16} s^{-1}) relies upon the transition-state (TS) expression of the Arrhenius law. The TS expression for the frequency factor notes $A = 2.7k_BT/h \exp(\Delta S^\ddagger/R)$, where $\Delta S^\ddagger$ is the total change of entropy in going from the biradical intermediate to the transition state. The rate parameters for photocycloreversion are presented both in Arrhenius and transition-state formulation (Table III). Benson and O'Neal have discussed extensively the computation of $\Delta S^\ddagger$ with the aid of simple bond additivity rules.[29] First application of this model to gas-phase unimolecular reactions with biradical intermediates shows that a barrier of at least 2 kcal/mol is expected to separate the biradical path from the concerted one. In addition, a value of $\Delta S^\ddagger \approx +8-10$ eu is assumed to be typical for a unimolecular reaction via biradical intermediate (e.g., thermolysis of cyclobutane) and a vlue of $\Delta S^\ddagger \approx 0$ to be typical for a concerted reaction (e.g., thermolysis of endodicyclopentadiene). It should be stressed that these parameters are not strictly comparable to liquid-phase reactions, although Turro et al.[30] have found similar $\Delta S^\ddagger$ values (+7-10 eu) for a liquid-phase thermolysis of POs via biradical intermediate. Indeed, the $\Delta S^\ddagger$ values included in Table III are of the same order, but the biradical pathways must be well distinguished for thermolysis and photolysis of POs from the view of correlation diagrams.

We will address now the question of difference in $\Delta S^\ddagger$ values found for the photocycloreversion of a few 9,10-POs. In comparison with other POs there is a higher entropy change in the biradical transition state of HOCDPO ($\Delta S^\ddagger \approx 11$ eu). Since the number of degrees of freedom of the TS is large, there is enough scope in the choice of parameters (e.g., translation, rotation, vibration modes, and symmetry change). The point at issue is whether the two C=O groups of HOCDPO contribute to the vibrational structure of TS in contrast to HECDPO. Our understanding about the disposal of thermal excess energy to BR decay is still incomplete.

Another important point deals with the transfer of thermal excess energy to solvent molecules. Intramolecular vibrational redistribution (IVR) of excess energy occurs in less than 1 ps and results in a "hot" molecule from which phonons may be transported to the solvent within a few picoseconds yielding thermally equilibrated molecules.[31] In general the dynamics of vibrational relaxation is a function of solvent and solute. Primary HOCD is produced "hot" as a result of the large exothermicity of photofragmentation (17000 cm^{-1}). The effect of internal temperature on HOCD can be seen distinctly in its transient absorption spectrum.[14] The extinction coefficient on the long-wavelength onset of S_1 is increased due to IVR of excess energy. The probe wavelength of HOCD excitation lies close to the $\approx$1700-cm^{-1} broad absorption maximum at 600 nm so that vibrational relaxation has only a minor effect on the measured time constant of 1.7 ps.

In our study on the photocycloreversion of 9,10-POs we have elucidated the reaction mechanism from the view of rate parameters and emphasized the importance of internal energy flow and energy transfer in solute-solvent collisions.

Conclusion

The photofragmentation of aromatic endoperoxides into singlet oxygen and the aromatic moiety occurs via a 1,6 biradical intermediate. The rate-determining step is the activation-controlled crossing of a 5-6 kcal/mol high barrier. The whole photoreaction proceeds on a singlet PES.

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(29) Benson, S. W.; O'Neal, H. E. *Kinetic data on gas phase unimolecular reactions*; Nat. Stand. Ref. Data Ser.; U.S., Natl. Bur. Stand., 1971; NSRDS-NBS 21.

(30) Turro, N. J.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218.

(31) Gottfried, N. H.; Seilmeier, A.; Kaiser, W. *Chem. Phys. Lett.* **1984**, *111*, 326.

Oscillations of $[HBrO_2]$, $[HBrO]$, $[Br^-]$, and $[Ce^{4+}]$ in the Belousov-Zhabotinsky Reaction Reconstructed from Quenching Experiments

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Simultaneous measurements of small-amplitude oscillations of $[Ce^{4+}]$ and $[Br^-]$ near a supercritical Hopf bifurcation of the Belousov-Zhabotinsky reaction have been used to reconstruct the oscillations of $[HBrO_2]$ and $[HBrO]$ from previously reported quenching experiments. The results provide direct and indirect experimental confirmation and improvement of amplitudes and phases of $[Br^-]$ and $[HBrO_2]$ determined from a previous "three-dimensional" reconstruction. Amplitudes and phases of $[HBrO]$ oscillations have not been reported before. Difficulties with the experimental determination of the $[Br^-]$ amplitude result in some uncertainty in the derived $[HBrO]$ amplitude, in particular.

Introduction

Quenching of chemical oscillations is an experimental method[1,2] for the determination of an (adjoint) eigenvector of the Jacobi matrix of an oscillatory chemical system.[3] It can be used near a supercritical Hopf bifurcation. The experimental method has been described in detail in ref 2 and will be reviewed below in this introduction.

Quenching data can be compared directly with models of a reaction, or it can be used to determine ("reconstruct") the amplitudes and phases of the oscillating concentrations of the species participating in a reaction. The theoretical basis for such uses of quenching data has been given in ref 3, which also gives an illustrative example showing the practical use of the method. We summarize the relevant results below.

The method has been used in ref 2 to reconstruct the oscillations of $[HBrO_2]$ and $[Br^-]$ in the Belousov-Zhabotinsky reaction from experimental quenching data with $[Ce^{4+}]$ monitored. The quenching data obtained there together with the oscillations of $[Ce^{4+}]$ allowed a determination of the oscillations of the con-

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(1) Hynne, F.; Graae Sørensen, P. *J. Phys. Chem.* **1987**, *91*, 6573.

(2) Graae Sørensen, P.; Hynne, F. *J. Phys. Chem.* **1989**, *93*, 5467.

(3) Hynne, F.; Graae Sørensen, P.; Nielsen, K. *J. Chem. Phys.* **1990**, *92*, 1747.

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