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Photoracemization of Bis(oxalato)(1,10-phenanthroline)chromate(III): Intensity and Wavelength Dependence Evidence for both Quartet and Doublet Pathways[1]

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Abstract: The title ion $(-)_D$-$[Cr(ox)_2phen]^-$ was irradiated in water at pH 6 (T = 25 °C) with laser wavelengths selected across the envelope of the first quartet band (514.5, 529, 575, 584, 600, 614, and 630 nm). Photoracemization was the only reaction observed. Quantum yield (Φ) *decreased* as light intensity (I) *increased*. At 600 nm, the results from I 0.001–0.030 einstein L^{-1} s^{-1} are governed by the expression $\Phi = 0.030 + [0.063/(1 + 143I)]$. Φ was independent of wavelength at $\lambda \leq$ 600 nm but decreased somewhat with λ increase at longer wavelengths. Φ also showed a dependence on complex concentration and small T dependence. Irradiation with right and left circularly polarized light at 584 nm where the circular dichroism of the initial complex is very close to zero gave a Φ_{RCPL}/Φ_{LCPL} ratio of 1.09 at 0.02 einstein L^{-1} s^{-1}. These results lend themselves to a consistent interpretation involving two distinct paths: an I-dependent path that originates from the doublet and an I-independent path that originates from the quartet. An optically active intermediate exists on the first path.

The photochemistry of Cr(III) complexes remains an area of very active interest after many studies because of the complexity of pathways and the opportunities afforded to address fundamental questions of photophysics and photochemistry. To summarize the situation most briefly, recent reviews record extensive evidence for prompt (picosecond) reactions from the first quartet ligand-field (LF) excited state, Q_1,[3,4] and also evidence for at least one reaction from the LF doublet manifold originating from the relatively long-lived lowest doublet, D.[5] In this second case, common pH dependence for thermal and photochemical pathways has suggested a common intermediate between photochemical and thermal substitution.

We have chosen the ion $(-)_D[Cr(ox)_2phen]^-$ for a study of photoracemization because of the simplicity of the reaction and the opportunity to use circularly polarized light as an additional experimental probe. The light source was an Ar ion laser supplemented by a dye laser with Rhodamine 6G. This permitted both careful exploration of wavelength (λ) dependence and, especially, intensity (I) dependence. In a complicated process, 2-photon work with laser sources is very valuable for elucidation of states that are not spectroscopically obvious. Finally, photoracemization of $[Cr(ox)_2phen]^-$ completes the series from $Cr(phen)_3^{3+}$ to $Cr(ox)_3^{3-}$ by presenting several surprises and an unusually rich mechanism problem, especially on the slow reaction path.

Experimental Section

Materials. $K(-)_D[Cr(ox)_2phen]\cdot 4H_2O$ was prepared and resolved by Broomhead's method.[6] The absorption spectrum in water matched that reported by Kaizaki et al.[7] Other reagents were common reagent grade materials from standard sources used as received. Water was distilled and deionized.

Procedures. Freshly prepared solutions (10.0 mL) of 1.00–3.00 × 10^{-3} complex were filtered through a 0.45-μm cellulose acetate filter and the pH was checked. These solutions were transferred to a water-jacketed circulating system at 5, 15 or 25 °C including a reservoir where O_2-free N_2 was bubbled through and a small-volume 10.0-cm polarimeter cell. The system circulated solution at 0.2 mL s^{-1} with a peristaltic pump. The circulating rate was such that neither cavitation and bubbles in the cell nor inner filter effects were significant. The polarimeter cell unit could be moved from a position in the irradiation beam to a Perkin-Elmer Model 241 automatic polarimeter without interruption of the thermostating system.

Irradiation at 514.5–630 nm was conducted by using a Coherent Radiation CR-6 SG Ar ion laser with a Model 590 dye laser with Rhodamine 6G. The beam diameters were 0.84 mm at 514.5 and 529 nm and 1.78 mm at all other wavelengths. Intensity was monitored two ways with good agreement. One was the popular reineckate chemical actinometry method.[8] The other involved measurement with a Coherent Radiation Model 210 Thermopile power meter. Power values were recorded before and after the cell and in comparison to the cell containing filtered water as a reference. Concentrations gave A = 0.3–0.7 in the 10-cm cell.

Our results confirm the quantum yields for the chemical actinometer and show that *it is free of intensity dependence under the conditions used* in the study of racemization (which is I dependent). The racemization process was followed by alternation of periods of irradiation (15–200 s) with periods of thermal racemization. A typical run is displayed in Figure 1. Runs using circularly polarized light used a quarter-wave plate centered on 589 nm.

Results

During the entire course of racemization shown in Figure 1, the visible and UV spectrum of the solution was closely monitored and remained constant. Also, the thermal racemization rate remained constant. Racemization is the only significant process at pH ~6.

The photoracemization shows an unusual intensity dependence that imposes stringent limits on the mechanistic discussion to follow. This dependence is unusual *but unambiguous*. Yield *decreases* with increasing intensity, approaching a high-intensity asymptote *different from zero*. Representative data obtained with 600-nm irradiation are shown in Figure 2. This dependence was confirmed at other wavelengths, as will emerge below. These can be fitted to the empirical equation 1 where ϕ_1 represents the

$$\phi = \phi_1 + \phi_2(I) = 0.030 + 0.063/(1 + 143I) \qquad (1)$$

intensity-independent yield and $\phi_2(I)$ the intensity-dependent term at [Cr(III)] = 2.05 × 10^{-3} M. The goodness of fit is illustrated by the reciprocal plot in Figure 3 that is described by eq 2 where the superscript 0 denotes a value approached as $I \rightarrow 0$.

$$\Phi_2^0/\Phi_2 = (\Phi^0 - \Phi_1)/(\Phi - \Phi_1) = 1 + 143I \qquad (2)$$

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[2] Visiting from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan.

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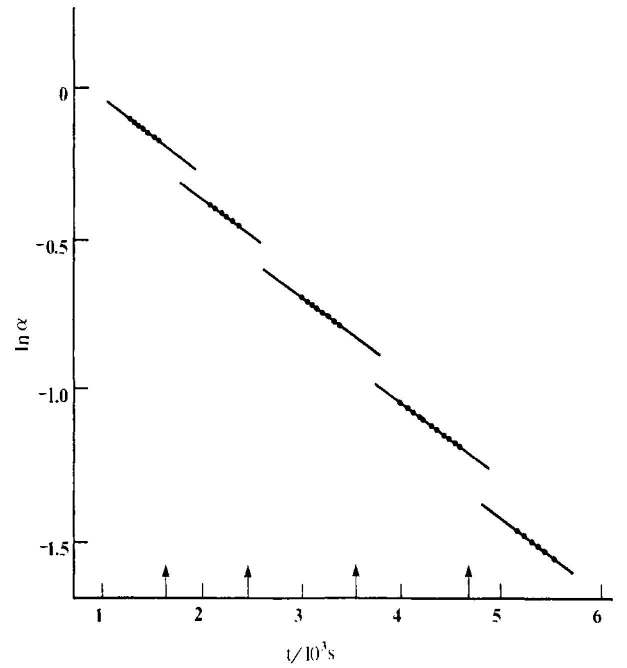

Figure 1. A typical first-order plot for thermal racemization interrupted by irradiations of 40–60 s at points indicated by arrows. The difference between the parallel lines showing thermal racemization served to indicate the progress of photoreaction.

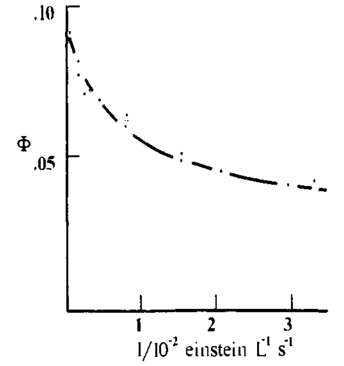

Figure 2. Dependence of quantum yield of the photoracemization on intensity [Cr] = 2.05 × 10^{-3} M, T = 25 °C, pH 6, and λ_{irr} 600 nm.

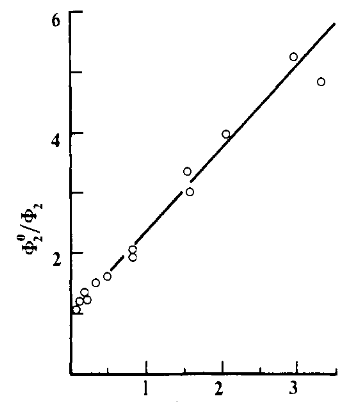

Figure 3. Reciprocal plot of data shown in Figure 2 with the best-fit line indicated.

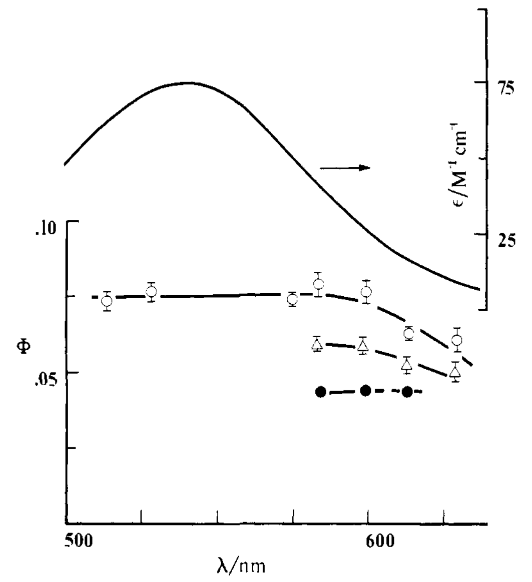

Figure 4. Wavelength dependence of quantum yields for racemization at several intensities. (○) 0.002 einstein L^{-1} s^{-1}, (△) 0.008 einstein L^{-1} s^{-1}, (●) 0.020 einstein L^{-1} s^{-1}. [Cr] 2.0 × 10^{-3} M, T = 25 °C, pH 6. The upper curve, which is referred to the ordinate on the right, gives the absorption spectrum of the complex.

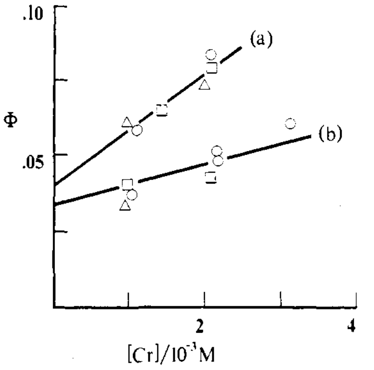

Figure 5. Dependence of photoracemization quantum yields on concentration of [Cr(phen)ox_2^-]. Curves are for intensities of 0.002 einstein L^{-1} s^{-1} (a) and 0.015 einstein L^{-1} s^{-1} (b). Points on the curves were obtained at 570, 585, and 600 nm. Wavelength was not a significant variable.

It is not unduly anticipating discussion to remark that the intensity dependence (decreasing Φ) implies an absorbing state or intermediate on the reaction path that retains optical activity. This was confirmed by experiments using circularly polarized light (CPL) at the wavelength of 584 nm where the CD of [Cr(ox)$_2$phen]$^-$ is reported to be near zero.[7] At an intensity of 0.0034 einstein L^{-1} s^{-1}, the ratio of Φ for right to left CPL, Φ_{RCPL}/Φ_{LCPL} = 1.00 ± 0.02 (four runs). At intensity between 0.019 and 0.026 einstein L^{-1} s^{-1}, Φ_{RCPL}/Φ_{LCPL} = 1.09 ± 0.04 (nine runs), which is significantly different from unity at the 95% confidence limit ([Cr] = 2.0 × 10^{-3} M, T = 25 °C).

The quantum yield for photoracemization exhibits a wavelength dependence of a sort that is becoming familiar in Cr(III) photochemistry. Wavelength dependence of $Q_1 \rightarrow D_1$ intersystem crossing or a reaction quantum yield frequently shows constant values throughout shorter wavelengths with a decline in the tail of Q_1.[9-11] This behavior is seen for the photoracemization yield in our system at *low* intensity, as Figure 4 shows. However, the second photon suppressed the pathway through the optically active intermediate at high intensity, and the wavelength dependence became undetectable.

Sriram et al.[12] demonstrated a self-quenching of long-lived Cr(III) D_1 states by the ^{4}A Cr(III) ground state. Consequently,

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Table I. Temperature Dependence of Photoracemization Quantum Yield for $(-)_D$-$[CrOX_2phen]^-$ in Water at Various Light Intensities at 600 nm[a]

	ϕ^b I/(einstein L^{-1} s^{-1})		
temp, °C	0.002	0.020	0.030
4.8	0.060, 0.065	0.032, 0.032	0.029
14.8	0.070	0.042	
25.0	0.077, 0.081	0.046	0.041

[a] $[Cr] \approx 2.05 \times 10^{-3}$ mol dm^{-3}. [b] ϕ values have ±0.003 uncertainty.

Table II. Effects of Additives on ϕ^a

additive	[additive]/10^{-3} M	μ	I/10^{-2} einstein L^{-1} s^{-1}	ϕ
KCl	9.6	0.01	0.13	0.071 ± 0.003
			1.55	0.050 ± 0.003
KI	32.6	0.03	0.15	0.074 ± 0.001
			1.69	0.047 ± 0.001
$K_3[Cr(CN)_6]$	2.1	0.008	1.52	0.050 ± 0.005
	10.5	0.03	0.12	0.067 ± 0.004
			2.70	0.043 ± 0.003
	39.4	0.12	0.12	0.073 ± 0.003
			2.51	0.037 ± 0.003

[a] Irradiation at 600 nm, $[Cr] = 2.0 \times 10^{-3}$ M.

Cr(III) systems must be checked for Cr(III) concentration dependence. In the present system modest Cr(III) concentration dependence was observed, consistent with an equation

$$\Phi = 0.030 + [\alpha/(1 + 143I)](k_1 + k_2[\mathrm{Cr(III)}]) \qquad (1')$$

where $k_1\alpha = 0.014$ and $k_2\alpha = 0.023 \times 10^3$ M^{-1}. Results at *two* light intensities and *several* λ's are shown in Figure 5. The result is that the Cr(III) ground state *enhances* racemization in a process associated with the intensity-dependent path.

Results on temperature dependenmce of photoracemization at several intensities are collected in Table I. In all cases, the apparent activation energy is small. No well-defined difference between the intensity-dependent and intensity-independent path is discernible.

A final series of experiments tested salt effects and effects of well-known doublet quenchers (I^-, $Cr(CN)_6^{3-}$). However, no significant effects were observed. Results are collected in Table II. The experimental points could be mapped onto results without such additives.

Discussion

The first observation is that, with the exception of temperature-dependence experiments, the distinction made in eq 1 and 1′ between the Φ_1 path and the $\Phi_2(I)$ path is reinforced throughout. Evidence for intensity dependence is general. The paths it distinguishes are supported by the supplementary evidence. The Φ_1 path is (1) intensity independent; (2) not demonstrably wavelength dependent; (3) not subject to circular polarization selectivity at 584 nm; (4) independent of Cr(III) concentration; and (5) only weakly temperature dependent.

Points 1, 3, and 4 show that the Φ_1 path is a direct racemization without the intervention of long-lived chemical intermediates or long-lived excited states. This suggests an *intramolecular* racemization originating from the short-lived Q_1 state. The second and more speculative part of this idea is supported by points 2, 4, and 5. The wavelength behavior seen here is very similar to that reported by Sandrini et al.[10] in the case of *trans*-$[Cr(en)_2(NCS)_2]^+$ if we assume that the wavelength dependence of the $\Phi_2(I)$ path is the parallel of the intersystem-crossing yield in ref 10. In the Sandrini et al. case, it could be argued that the unquenchable path was directly from Q_1. (Their conclusion was secured with doublet quencher experiments, but we obtained negative result from attempts to quench with I^- and $Cr(CN)_6^{3-}$, which might be expected to be less effective for our anionic complex.) In our case, the lack of a large apparent activation energy matches the behavior of the nonquenchable part of the reaction of $[Cr(phen)_2ox]^+$ (E_a = 2.2 kcal mol^{-1}) and contrasts with an apparent activation energy ~10 kcal mol^{-1} for the contribution to racemization, which was quenchable with I^- in the case of $[Cr(phen)_2ox]^+$.[13]

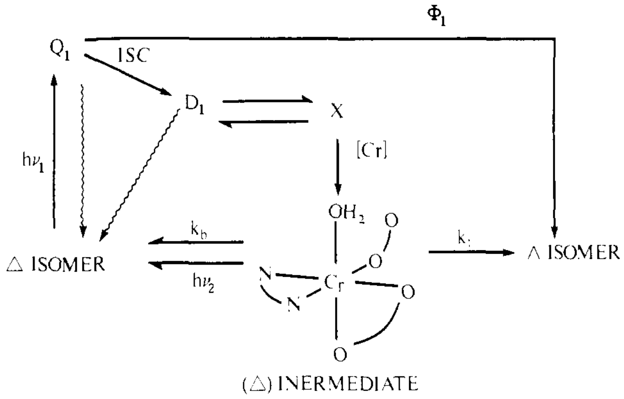
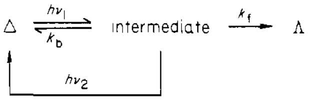


Figure 6. Summary of the mechanism established by the experiments with specific suggestions as to the nature of the intermediate and the excited state from which the reaction paths originate. It is possible that the state labeled X is either a doublet of the intermediate or possibly a seven-coordinate precursor to the intermediate. Note that results demand only stereospecificity to the intermediate. It could be the opposite isomer. The figure is specific for clarity only.

We therefore propose that the Φ_1 path is a direct *intramolecular* racemization. Most probably, it is a reaction from Q_1. (The lack of well-defined wavelength dependence does not suggest the special dependence on initial degree of vibronic excitation reported for $Cr(phen)_3^{3+}$.[11])

We now turn our attention to the $\Phi_2(I)$ path. The first question to address is the interpretation of the I dependence. What is the role of the second photon? We can write eq 3 as a starting point



(3)

where Δ represents the initial enantiomer and Λ the isomerized enantiomer. $h\nu_1$ designates the first photon, $h\nu_2$ the second, and k_f and k_b thermal rate constants from the intermediate. When one attempts to identify the intermediate, the intensity dependence can be subjected to quantitative interpretation. If Φ_{int} is the quantum yield for formation of the intermediate using the photon $h\nu_1$, then $\Phi_2(I)$ is given by eq 4 where Φ' is the quantum yield

$$\Phi_2 = \Phi_{int} \frac{k_f}{k_f + k_b + I\epsilon'\delta\Phi} \qquad (4)$$

for returning the intermediate to the initial enantiomer (supression by increased intensity). In (4), ϵ' is the molar absorptivity and δ is the pathlength. If one expresses the equation in terms of the lifetime of the intermediate $\tau' = 1/(k_f + k_b)$, eq 4 yields eq 5,

$$(\Phi_2^0/\Phi_2) = 1 + \tau'\Delta'\delta\Phi'I \qquad (5)$$

which may be compared to the experimental expression eq 2. This comparison yields the result that $\tau'\Delta'\delta\Phi'$ = 143 L $einstein^{-1}$ where δ = 10 cm. If $\epsilon' < 10^5$ and $\Phi' < 1$, then $\tau' > 10^{-4}$ s. Since ϵ' cannot be more than about 10^3 in a Cr(III) complex, the best estimate of the order of magnitude of τ' is $\geq 10^{-2}$ s. The lifetime of the intermediate is clearly too long for the intermediate to be simply the doublet, D_1, of the initial complex. The longest lifetime known for a D_1 is $\leq 10^{-3}$ s, and well-established data make it clear that

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a much shorter value would be expected for D_1 of the present complex.[5]

In contrast to the negative indication with respect to a D_1 assignment, an alternative is quite attractive. A one-end dechelated-oxalate species with a water on the vacated-coordination position, as shown in Figure 6, is attractive. In this case, τ' would be associated with the rate constants for reclosing of the oxalate chelate ring with substitution for a water ligand. Since it is known that oxoanions form Cr(III) complexes relatively rapidly without fission of a metal–oxygen bond,[14] a value of τ' near 1 s would be quite reasonable. This would correspond to a value of $\epsilon' \simeq 10^2$ and $\Phi' \simeq 0.1$. These are reasonable values since the absorptivity of the aquo-substituted intermediate would be assignable to a ligand-field band similar to those of the starting complex and the quantum yield, Φ', is for a process similar to Φ_{int}.

The aquo intermediate is produced with a large stereospecificity as indicated by the nearly complete suppression of the $\Phi_2(I)$ path of racemization at high *I and the success of the CPL* experiment. Since the second step governed by k_f is essentially the same as that in the fairly well-studied thermal racemization,[15] we have chosen to associate it with inversion. The opposite stereospecificity is also possible since the results demand only specificity.

The wavelength dependence is the clue to the excited-state origin of the reaction leading to the intermediate on the $\Phi_2(I)$ path. The yield declines beyond 600 nm, which has been shown to be a characteristic of a number of intersystem-crossing processes in Cr(III).[9-11] The implication is clearly that the $\Phi_2(I)$ path originates from D_1.

In addition, Figure 6 suggests that the reaction from D_1 leads to a quenchable intermediate (plausibly a doublet). The need for this suggestion is that the ground-state "quenching" shown in Figure 5 promotes racemization. That is, it quenches an initial product to a state farther advanced on the reaction coordinate. The ground-state quenching also excludes the possibility of formation of the intermediate from Q_1. We emphasize that the argument here rests on a single phenomemon that could not be confirmed with other quenchers.

Conclusions

The overall mechanism of Figure 6 shows *more variety* in a single reaction than any other Cr(III) system that has been studied. Still, all aspects except the interesting, well-documented, intensity dependence and CPL selectivity have precedents in the Cr(III) literature. Nonetheless, there are specific experimental results requiring *at least* this many *distinct* features in the mechanism! What we can do finally is ask whether the particular suggestions here are consistent with our current theoretical understanding of Cr(III) photochemistry.[3,4]

With respect to the Φ_1 path, the emphasis given here to a *one-step* intramolecular process does not seem entirely consistent with multistep-dissociative models such as the Vanquickenborne–Ceulemans approach.[3] Rather the present results would tend to lend some support to Kirk's conclusion[3] that a one-step associative version of the model would be useful. From the alternative prompt reaction viewpoint developed by Hollebone,[4] the question becomes the nature of the vibration coordinates excited during excitation since they are postulated to determine prompt relaxation options. For the quartet–quartet transition the octapole rule requires the vibronic coupling to involve the bases $|3t_1u_0\rangle$, called the buckle mode,[4] or $|3t_2u_0\rangle$, called the twist mode.[4] This last mode is just what is required for a twist-type isomerization.[4]

The large stereospecificity in the $\Phi_2(I)$ path implies that the D_1 state reacts via attack by water in an I_a associative step. The assignment of the reaction to D_1 suggests the cis-attack stereochemistry of Figure 6 since there is some precedent for trans attack on Q_1.[3] Thus, the mechanism proposed in Figure 6 agrees with the main lines of thinking about the theory of Cr(III) photochemistry as recently critically reviewed,[3-5] including the latest nuances.

Registry No. $\mathrm{K}(-)_{\mathrm{D}}[\mathrm{Cr(ox)_2phen}]$, 23594-46-9; KCl, 7447-40-7; KI, 7681-11-0; $\mathrm{K_3[Cr(CN)_6]}$, 13601-11-1.

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Serial Cyclization: Studies in the Mechanism and Stereochemistry of Peroxy Radical Cyclization[1]

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Abstract: In this study two unsaturated hydroperoxides, model compounds for natural rubber, polyunsaturated isoprenoids such as polyprenols, and polybutadiene, were exposed to initiators in the presence of oxygen. The products of these reactions were isolated and found to be cyclic peroxides that could be produced by a series of reactions involving peroxy radical cyclizations followed by trapping of molecular oxygen to form new peroxy radicals.

Autoxidation, the low-temperature reaction between molecular oxygen and hydrocarbons, is one of the most general reactions in organic chemistry. Free radicals are frequently generated in all systems exposed to the atmosphere,[2] and the reaction of these radicals with molecular oxygen to form peroxy radicals is extremely rapid. The formation and subsequent reaction of these peroxy radicals are key steps in a wide variety of biological and nonbiological systems.

The degradation of rubber, polybutadiene, and isoprenoid natural products such as squalene, ubiquinones, other prenyl derivatives, etc. involves peroxy radical intermediates.[3-8] Fur-

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