# Direct Kinetic Observation of the Chemiexcitation Step in Peroxyoxalate Chemiluminescence

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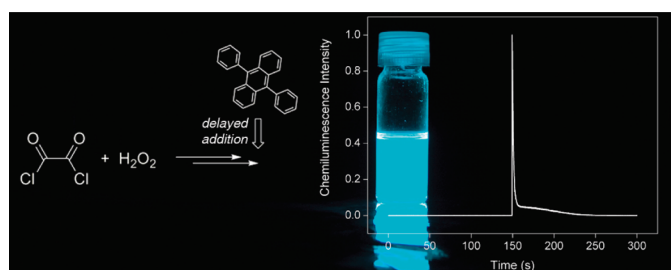
A high-energy intermediate in the peroxyoxalate reaction can be accumulated at room temperature under specific reaction conditions and in the absence of any reducing agent in up to micromolar concentrations. Bimolecular interaction of this intermediate, accumulated in the reaction of oxalyl chloride with hydrogen peroxide, with an activator (highly fluorescent aromatic hydrocarbons with low oxidation potential) added in delay shows unequivocally that this intermediate is responsible for chemiexcitation of the activator. Activation parameters for the unimolecular decomposition of this intermediate ($\Delta H^{\ddagger} = 11.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -23.2$ cal mol^{-1} K^{-1}) and for its bimolecular reaction with 9,10-diphenylanthracene ($\Delta H^{\ddagger} = 4.2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -26.9$ cal mol^{-1} K^{-1}) show that this intermediate is much less stable than typical 1,2-dioxetanes and 1,2-dioxetanones and demonstrate its highly favored interaction with the activator. Therefore, it can be inferred that structural characterization of the high-energy intermediate in the presence of an activator must be highly improbable. The observed linear free-energy correlation between the catalytic rate constants and the oxidation potentials of several activators definitely confirms the occurrence of the chemically initiated electron-exchange luminescence (CIEEL) mechanism in the chemiexcitation step of the peroxyoxalate system.

Introduction

The peroxyoxalate system is one of the most efficient nonenzymatic chemiluminescent reactions known, showing quantum efficiency of up to 50%.[1,2] The "bluish-white" light, first observed by Chandross from the reaction between oxalyl chloride and hydrogen peroxide in the presence of 9,10-diphenylanthracene (DPA),[3] has inspired generations of scientists to investigate the reaction mechanism and to search for new substrates and experimental conditions to improve emission efficiency.[4]

Although the system is widely used in ultrasensitive analytical applications,[5] the mechanism of the peroxyoxalate reaction is still not completely understood. It is established that hydrogen peroxide reacts with the oxalate to form a peracid intermediate, which by intramolecular cyclization produces a cyclic peroxide as high-energy intermediate (HEI).[4,6] This HEI can undergo thermal decomposition or react with an easily oxidizable highly fluorescent compound,

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(3) Chandross, E. A. *Tetrahedron Lett.* **1963**, *4*, 761–765.
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SCHEME 1. Elementary Peroxyoxalate Reaction Mechanism
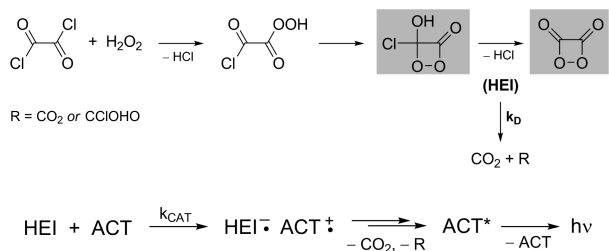
hereafter called activator (ACT), resulting in chemiluminescence emission apparently through the chemically initiated electron-exchange luminescence (CIEEL) mechanism (Scheme 1).[1,7,8]

Mechanistic studies on the peroxyoxalate reaction can be divided into three main subjects: (i) the kinetics of HEI formation (before chemiexcitation); (ii) the elucidation of the structure of the HEI; and (iii) the mechanism of chemiexcitation.[4] Although our group and others have extensively explored the formation kinetics and nature of the HEI, its structure is still controversial[9−12] and direct experimental insight into the chemiexcitation step (i.e., transformation of the "chemical" energy into electronic excitation energy) is scarce.[1,13,14] Briefly, it is known that[4] (i) in the presence of any reducing agents, such as transition metal or other easily oxidizable substances, any peroxidic intermediate should be rapidly destroyed and is not expected to accumulate;[2,4,8] (ii) a peracid intermediate is formed by nucleophilic attack of hydrogen peroxide to the oxalic carbonyl, although this peracid is not the HEI as it does not interact directly with activators;[6,15] (iii) even in the absence of an ACT, the HEI is unstable and chemical trapping was not achieved until now.[12]

Recently, 1,2-dioxetanedione has apparently been identified by Barnett et al. using ^{13}C NMR spectroscopy as an intermediate in the peroxyoxalate reaction; additionally, the occurrence of an oxalate biradical intermediate in the reaction course was evidenced by EPR spectroscopy.[9,10] These experiments have been carried out at low temperatures (< 200 K), due to the low stability of the intermediates involved,[10] however, *surprisingly, in the presence of an activator*, which is supposed to lower the lifetime of any HEI.[9,10] Consequently, although these experiments may provide evidence for the structure of intermediates in the peroxyoxalate reaction and indicate the occurrence of radical intermediates in this transformation, they do not directly contribute

to clarify the mechanism of the chemiexcitation step in this reaction sequence, as they do not correlate spectroscopic data on intermediate structures to chemiexcitation; that is, there is no unequivocal evidence that the intermediates detected are those responsible for chemiexcitation through reaction with the ACT. In their early works, Rauhut and collaborators were able to detect a volatile metastable intermediate,[2] formed during the peroxyoxalate reaction in the absence of an activator; however, this observation could not be confirmed by other research groups.[14,17]

Herewith we describe, for the first time, the direct kinetic observation of the chemiexcitation step in peroxyoxalate chemiluminescence. In adequate reaction conditions, a HEI accumulates at room temperature in the reaction between oxalyl chloride and hydrogen peroxide,[2,3,18] making it possible to directly measure the rate constants for the interaction of this intermediate with added activators. This arrangement permits the complete kinetic characterization of this process, allowing the determination of activation parameters and the confirmation of the occurrence of the CIEEL mechanism in the chemiexcitation step.

Results and Discussion

The reaction of oxalyl chloride with hydrogen peroxide, the original peroxyoxalate system,[3] was used to accumulate a metastable high-energy intermediate and to observe its direct interaction with an activator added in delay.[19] The emission kinetics of this system is reasonably fast at room temperature, even in the absence of base catalysis. Additionally, it is known that the presence of base lowers the emission quantum yields of the peroxyoxalate reaction[1,4] due to its destructive interaction with the HEI, preventing excited-state formation.[16]

The reaction system with 9,10-diphenylanthracene (DPA) as activator present from the start of the reaction (standard system) results in low-intensity chemiluminescence emission, corresponding to the fluorescence of the activator (Figure 1). However, delayed addition of DPA to the reaction system (delayed system) gives rise to an intense flash of light, which decays within a few seconds (Figure 1). The emission intensity of this light flash is at least 1 order of magnitude higher than the maximum intensity of the standard system. The execution of this experiment requires the exhaustive purification of reactants and solvents and the elimination of any trace of metals from the glassware and injection syringes; otherwise, no light flash is observed (see Experimental Section).

The observed rate constant (k_{obs}), obtained upon delayed DPA addition, proved to depend on its final concentration, indicating the occurrence of a bimolecular interaction between the HEI and DPA, which is in agreement with the occurrence of the CIEEL mechanism in the chemiexcitation step and excludes the ACT excitation by an electronic energy transfer (Scheme 1). The HEI decomposition constant in the absence of activator (k_D) and the catalytic rate constant

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(19) Ethyl acetate is an ideal solvent to perform this study since it has been used before in various peroxyoxalate systems by our group;[1,4,13,16] moreover, it can be purified adequately.
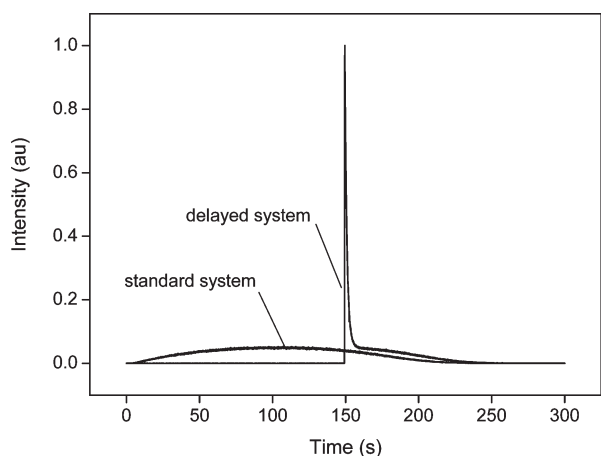
FIGURE 1. Kinetic emission profile of the peroxyoxalate system. Standard system: oxalyl chloride (1.0 mmol L^{-1}), H$_2$O$_2$ (4.0 mmol L^{-1}), DPA (0.2 mmol L^{-1}), in ethyl acetate at 20 °C. Delayed system: DPA was added 150 s after the start of the reaction.

(k_{CAT}) can be calculated from the linear dependence of the observed decay rate constant (k_{obs}) on the concentration of the activator added in delay (Figure 2, Scheme 1, and Supporting Information Table S1): $k_D = 0.096 \pm 0.012$ s^{-1}, $k_{CAT} = (3.74 \pm 0.07) \times 10^3$ L mol^{-1} s^{-1} ($r = 0.9994$).[20,21]

Changing the delay time before the addition of constant concentrations of DPA leads to the observation of different initial emission intensities (I_0) (Figure 3), which correspond to the rate of interaction between the ACT and the HEI. Consequently, it is related to the concentrations of both, as well as, the singlet excited-state formation quantum yield (Φ_S) and the fluorescence emission quantum yield (Φ_{Fl}) of the ACT (eq 1). As these yields are constant, the value of I_0 observed upon addition of a constant amount of activator is directly proportional to the HEI concentration (eq 1).

$$I_0 = k_{CAT}[ACT][HEI]\Phi_S\Phi_{Fl} \qquad (1)$$

The chemiluminescence intensities initially measured by the detection system in arbitrary units were transformed into the absolute intensity units, Einstein per second (E s^{-1}), by using the aqueous luminol standard.[4] Therefore, the concentration of the HEI corresponding to the emission intensity (I_0), observed for a specific addition delay time, can roughly be estimated from eq 1, as the quantum yields (Φ_S and Φ_{Fl}) are known from studies on a peroxyoxalate system in very similar experimental conditions,[1] and k_{CAT} has been determined exactly in the present work (see Supporting Information). The time course of the [HEI] in the absence of the ACT is different from that in its presence, as can be seen from a comparison of the I_0 values obtained upon delayed ACT addition with the emission intensity time course of the complete system, which also reflects the [HEI] concentration at any time (Figure 3 and Supporting Information Table S2). The additional ordinate scale expressed as estimated high-energy intermediate concentration

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(20) All linear regressions were carried out using a fitting function which modifies weighting of data points based on their relative standard deviations.

(21) The intercept of the linear plots of observed rate constants (k_{obs}) with the activator (ACT) concentration corresponds to the unimolecular decomposition rate constant (k_D) of the HEI, and the angular coefficient to the bimolecular catalytic rate constant (k_{CAT}), of the interaction between the HEI and the ACT.
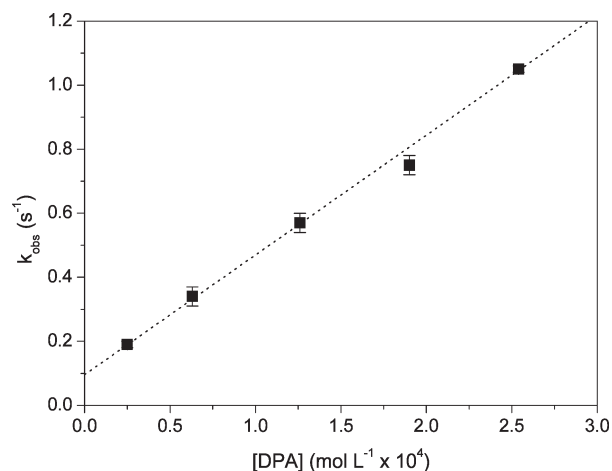
FIGURE 2. Linear correlation of the observed rate constants (k_{obs}) and the activator concentration in the delayed (150 s) addition of 9,10-diphenylanthracene (DPA) to oxalyl chloride and hydrogen peroxide. [Oxalyl chloride] = 1.0 mmol L^{-1}, [H$_2$O$_2$] = 4.0 mmol L^{-1}, at 20 °C in ethyl acetate.
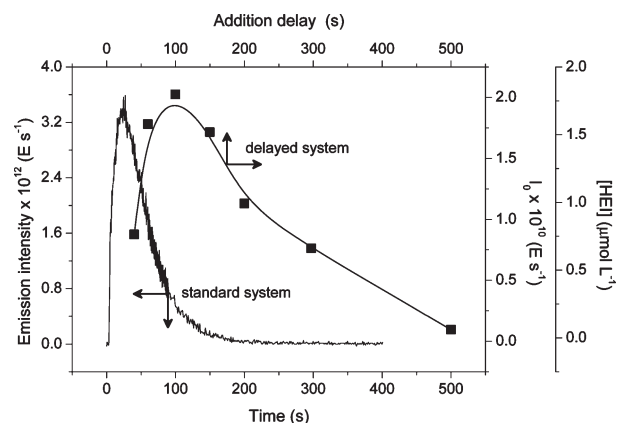

FIGURE 3. Emission intensity profiles of the standard and delayed systems with DPA and estimated high-energy intermediate time course. See Figure 1 for experimental conditions.

(Figure 3) obtained according to eq 1 shows that the maximum HEI concentration can reach up to micromolar values ([HEI]$_{max}$ ∼ 2 μmol L^{-1}). Additionally, from the relative emission intensities of the standard and delayed system, it can be estimated that the maximum [HEI] in the standard system is at least 50 times lower than that in the delayed system (Figure 3), making it extremely improbable that any HEI might be detected and characterized in the presence of an activator as claimed in the literature.[9,10]

For the determination of the activation parameters in the reaction of the HEI with DPA, the emission intensity decay upon delayed addition of different DPA concentrations was measured in the temperature range from 5 to 25 °C. The rate constants k_D and k_{CAT} were obtained from the linear correlation of the observed rate constants (k_{obs}) with the [DPA] for each reaction temperature (Figure 4 and Supporting Information Table S3).

The Eyring plots for the obtained rate constants k_D and k_{CAT} (Supporting Information Table S3) show very good
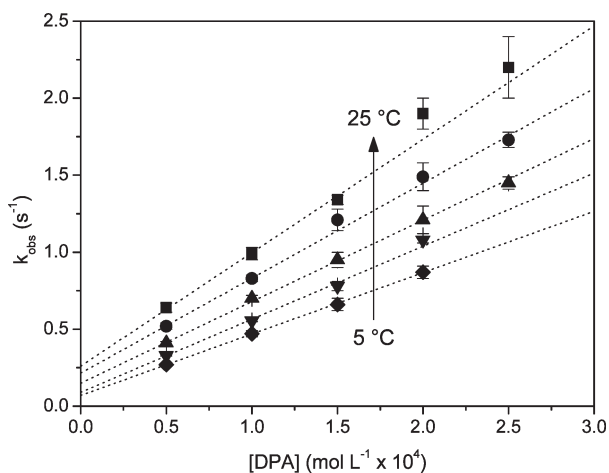
FIGURE 4. Linear correlation of the observed rate constants (k_{obs}) with the 9,10-diphenylanthracene (DPA) concentration at 5, 10, 15, 20, and 25 °C. [Oxalyl chloride] = 1.0 mmol L^{-1}, [H_2O_2] = 4.0 mmol L^{-1}, in ethyl acetate; DPA was added with a delay of 150 s.

FIGURE 5. Eyring plots for the unimolecular decomposition rate constant (k_D, r = 0.993) and the bimolecular catalytic rate constant (k_{CAT}, r = 0.995) of the reaction between the HEI and DPA added in delay (150 s). See Figure 4 for experimental conditions.

linearity (r > 0.99), permitting the determination of the activation parameters for the unimolecular decomposition of the HEI as well as for the interaction of this intermediate with the activator DPA (Figure 5).

The activation parameters for the unimolecular decomposition show that the HEI in the peroxyoxalate reaction is much less stable than other cyclic four-membered peroxides as 1,2-dioxetanes and α-peroxylactones, mainly reflected in the activation enthalpy, which is 8 kcal mol^{-1} lower than that for the most studied α-peroxylactone, dimethyl-1,2-dioxetanone (Table 1).[4,7,8] Interestingly, the HEI appears to suffer decomposition by bimolecular processes, as indicated by the relatively low activation entropy, when compared to that of the other cyclic peroxides. The half-lifetimes ($t_{1/2}$) calculated from the $\Delta G^{\ddagger}$ values clearly illustrate the much lower stability of the HEI occurring in peroxyoxalate reaction, as compared to the other cyclic peroxides, with a $t_{1/2}$ value about 2 orders of magnitude lower than that of the unsubstituted 1,2-dioxetane,[22,23] one of the least stable dioxetane derivatives isolated, and dimethyl-1,2-dioxetanone, the most studied α-peroxylactone derivative (Table 1). This fact may explain why this intermediate has not yet been unequivocally identified, although several attempts,[2,11,12,17] including recent studies,[9,10] have been performed.

The very low activation enthalpy for the DPA-catalyzed decomposition, as compared to that determined for the reaction of dimethyl-1,2-dioxetanone with DPA[24] (Table 1), clearly indicates the extremely high reactivity of the HEI toward the ACT as compared to that of dimethyl-1,2-dioxetanone, showing the huge difference of more than 10 kcal mol^{-1} in the activation enthalpy (Table 1). This is best illustrated by the lifetime values in the presence of millimolar concentrations of activator, which are more than 3 orders of magnitude
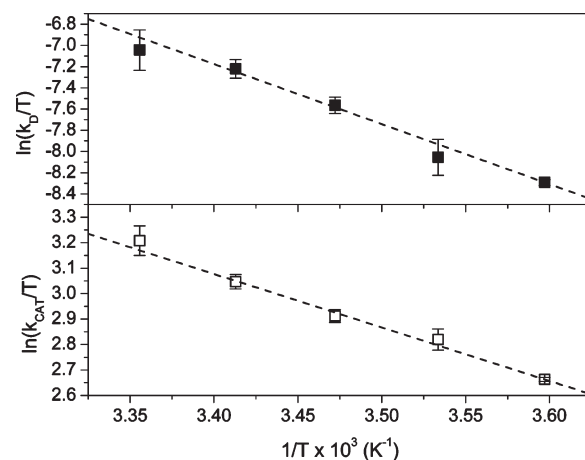
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lower for the peroxyoxalate HEI than for the α-peroxylactone derivative (Table 1). It should also be pointed out clearly that the peroxyoxalate HEI lifetime in the presence of the activator is more than 1 order of magnitude lower than that in its absence. Furthermore, the highly negative activation entropy clearly indicates the occurrence of a bimolecular reaction between the added activator and the HEI, in excellent agreement with the postulated CIEEL mechanism.[7] As the peroxyoxalate system is the only highly efficient *intermolecular* chemiluminescence transformation with proven high quantum yields, this result is of outstanding importance with respect to the validation of the CIEEL mechanism. One of the reasons of the high efficiency of this chemiexcitation mechanism in the peroxyoxalate system, as compared to the catalyzed decomposition of isolable cyclic peroxides, may be due to this extremely high reactivity of the HEI toward activators as DPA.[4]

In order to verify the possible involvement of electron transfer steps in the chemiexcitation mechanism of the peroxyoxalate reaction, the *delayed system* was studied using ACTs with different half-wave oxidation potentials ($E_{p/2}^{ox}$), ranging from 0.6 to 1.5 V vs SCE.[1] The values of k_D and k_{CAT} were calculated for each ACT from the linear dependence of k_{obs} (Supporting Information Table S4) with the activator concentration (Figure 6 and Table 2).

The decomposition rate constants (k_D) do not vary significantly with the nature of the ACT, and the mean value for all of the ACTs utilized is k_D = 0.033 ± 0.011 s^{-1}, indicating that these values really correspond to the unimolecular (including "impurity catalyzed") decomposition of the HEI, which is expected to be independent of the nature and concentration of the activator. Contrarily, the catalytic rate constants (k_{CAT}) show a drastic dependence on the ACT's oxidation potential, spanning a range of almost 4 orders of magnitude for a potential variation of less than 0.9 V (Table 1). The highest value is obtained for rubrene, possessing the lowest oxidation potential, and PPO with the highest potential shows the lowest k_{CAT} value. The free-energy correlation of k_{CAT} with $E_{p/2}^{ox}$ leads to a good linear correlation (r = 0.95, Figure 7), from which the

TABLE 1. Activation Parameters for the Unimolecular and Catalyzed Decomposition of the High-Energy Intermediate in Peroxyoxalate Reaction (as well as for some important isolable cyclic organic peroxides)

system	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})[a]	$t_{1/2}$ (s) [a,b]
	unimolecular decomposition (k_D)			
peroxyoxalate/HEI	11.2 ± 0.4	-23.2 ± 0.8	18.2 ± 0.6	2.3
dimethyl-1,2-dioxetanone[24]	19.2 ± 0.2	-8.2 ± 0.5	21.6 ± 0.3	720
1,2-dioxetane[22,23]	19.5 ± 0.3	-3.0 ± 0.2	20.4 ± 0.3	95
tetramethyl-1,2-dioxetane[8,25]	26.0 ± 0.1	3.7 ± 0.3	25.8 ± 0.2	860 000
	catalyzed decomposition (k_{CAT})			
peroxyoxalate/HEI	4.2 ± 0.1	-26.9 ± 0.2	12.2 ± 0.1	0.093[c]
dimethyl-1,2-dioxetanone[24]	15.0 ± 0.4	-5.7 ± 1.2	16.7 ± 7.6	180[c]

[a] At 25 °C. [b] Calculated from the $\Delta G^{\ddagger}$ values. [c] Calculated for [DPA] = 1.0 mmol L^{-1} from the bimolecular rate constant obtained from the $\Delta G^{\ddagger}$ value.
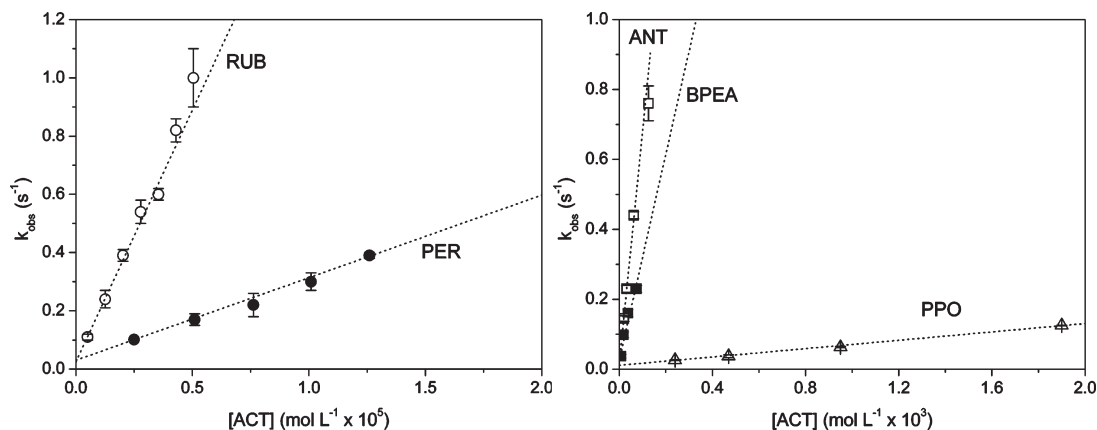
FIGURE 6. Linear correlation of the observed rate constants (k_{obs}) and the activator concentration in the delayed (150 s) addition of rubrene (RUB), perylene (PER), 9,10-bis(phenylethynyl)anthracene (BPEA), anthracene (ANT), and 2,5-diphenyloxazole (PPO) to oxalyl chloride and hydrogen peroxide. [Oxalyl chloride] = 1.0 mmol L^{-1}, [H$_2$O$_2$] = 4.0 mmol L^{-1}, at 20 °C in ethyl acetate.

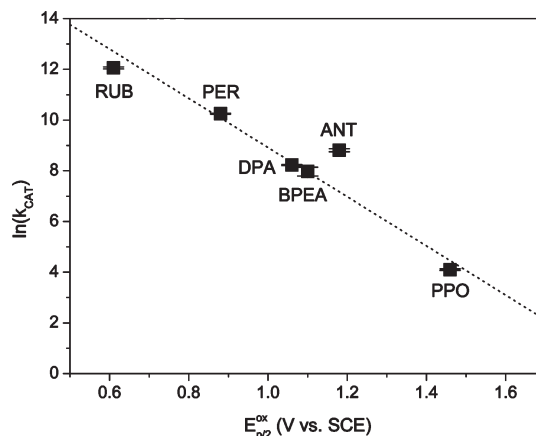**TABLE 2.** Kinetic Constants Calculated from the Peroxyoxalate Reaction upon Delayed Addition (150 s) of Different ACTs[a]

ACT	$E_{p/2}^{ox}$ (V vs SCE)	k_{CAT} (L mol^{-1} s^{-1})	$k_D \times 10^2$ (s^{-1})
RUB	0.61	$(1.7 \pm 0.1) \times 10^5$	2.4 ± 1.4
PER	0.88	$(2.8 \pm 0.1) \times 10^4$	3.0 ± 0.1
DPA	1.06	$(3.7 \pm 0.1) \times 10^3$	9.6 ± 1.2
BPEA	1.10	$(2.9 \pm 0.5) \times 10^3$	2.4 ± 1.5
ANT	1.18	$(6.7 \pm 0.4) \times 10^3$	1.2 ± 1.8
PPO	1.46	$(6.0 \pm 0.2) \times 10^1$	1.1 ± 0.2

[a] [Oxalyl chloride] = 1.0 mmol L^{-1}, [H$_2$O$_2$] = 4.0 mmol L^{-1}, 20 °C. RUB: rubrene, PER: perylene, DPA: 9,10-diphenylanthracene, BPEA: 9,10-bis(phenylethynyl)anthracene, ANT: anthracene, PPO: 2,5-diphenyloxazole.

electron transfer coefficient (α) can be obtained according to the Marcus equation (eq 2).[26,27]

$$\ln(k_{CAT}) = \ln A + \alpha \left(\frac{e^2}{R_o \varepsilon RT} + \frac{E_{HEI}^{red}}{RT} \right) - \left(\frac{\alpha}{RT} \right) E_{p/2}^{ox} \quad (2)$$

where α is the electron transfer coefficient; R is the gas constant; T is temperature; $E_{p/2}^{ox}$ is the activator oxidation potential; E_{HEI}^{red} is the high-energy intermediate reduction potential, which is constant; e is electron charge; R_o is the distance between radical ions in charge transfer complexes; and ε is the dielectric constant of the solvent.

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FIGURE 7. Linear free-energy correlation of the catalytic rate constants (k_{CAT}) and the ACT's oxidation potentials ($E_{p/2}^{ox}$) in the interaction between the HEI and the ACT (r = 0.95). [Oxalyl chloride] = 1.0 mmol L^{-1}, [H$_2$O$_2$] = 4.0 mmol L^{-1}, 20 °C. RUB: rubrene, PER: perylene, BPEA: 9,10-bis(phenylethynyl)anthracene, ANT: anthracene, PPO: 2,5-diphenyloxazole.

This result clearly indicates the occurrence of an electron transfer from the ACT to the HEI as predicted by the CIEEL mechanism (Scheme 1).[1,4,7,8] The value of $\alpha = 0.23 \pm 0.02$, calculated in this work *from direct kinetic measurements*, points to an early transition state with respect to the electron transfer and presumably also to O−O bond cleavage as these two steps are supposed to occur concomitantly.[4,27]

This α value is in agreement with that reported in the literature for several CIEEL systems, including variations of the peroxyoxalate reaction[1,13] and decomposition of isolated cyclic peroxides,[7,8,25,28−32] which are typically in the range of 0.1−0.3.[4]

Conclusions

This work provides unequivocal *direct* kinetic evidence that (i) a HEI can accumulate in the reaction between oxalyl chloride and hydrogen peroxide in the absence of an activator; (ii) this intermediate is much less stable than isolable chemiluminescent cyclic peroxides, but extremely reactive toward appropriate activators; (iii) the CIEEL mechanism actually occurs in the chemiexcitation step; and (iv) the HEI can be accumulated in the reaction system at room temperature in the micromolar concentration range, a fact which might make it prone to spectroscopic detection and characterization.

Experimental Section

Kinetic Assays. The extensively purified (see Supporting Information) solvent ethyl acetate was transferred under nitrogen to a 10 mm quartz cuvette containing a magnetic stirrer and thermostatted for 15 min in the fluorimeter cell holder. An appropriate volume of the hydrogen peroxide stock solution was added (final concentration = 4.0 mmol L^{-1}), and the reaction was started with an appropriate volume of the oxalyl chloride stock solution (final concentration = 1.0 mmol L^{-1}).

After a defined delay time, the activator (ACT) was added to the reaction system, resulting in an intense, easily visible flash of light, characteristic for the delayed addition system. The complete procedure was carried out in the dark, and data acquisition was started after the addition of H_2O_2. For the experiment to be successful, all reagents and solvents have to be of extremely high purity and all solutions have to be handled under dry, inert atmosphere. The addition of the ACT solution must be fast, with the syringe needle away from the magnetic stirrer to not accidentally stop the stirring during the moment of addition. Furthermore, all cuvettes have to be washed several times between assays, using a sequence of toluene, ethanol, acetone, and ethyl acetate (specially treated for the kinetic measurements) washings and dried under a nitrogen flow. The injection syringes were also washed with ethyl acetate and dried between injections, taking special care with the one used for the oxalyl chloride solution. Therefore, the execution of the experiments demands a highly trained operator. Using these precautions, it was possible to obtain reproducible kinetic data with this simple methodology, even for rate constants of $k_{obs} \sim 1$ s^{-1}, with standard deviations lower than 10%.[33]

Supporting Information Available: Detailed purification of chemicals, determination of the high-energy intermediate (HEI) concentration, and tables containing data corresponding to Figures 2, 3, 5, and 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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