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KINETIC STUDIES ON THE CHEMILUMINESCENT DECOMPOSITION OF AN ISOLATED INTERMEDIATE IN THE PEROXYOXALATE REACTION†

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The peroxyoxalate system undergoes one of the most efficient chemiluminescence reactions and is the only one considered to involve an intermolecular chemically initiated electron exchange luminescence mechanism, with proven high efficiency. Several reactive intermediates have been proposed, which, upon interaction with a fluorescent activator, lead to excited-state generation. The synthesis and spectral characterization of 4-chlorophenyl *O,O*-hydrogen monoperoxyoxalate (1), a compound analogous to one of the proposed reactive intermediates, was recently reported. Here the results of a kinetic study on the chemiluminescent decomposition of this peracid 1, catalyzed by oxygen bases (potassium hydroxide, potassium *tert*-butoxide and potassium *p*-chlorophenolate) or nitrogen bases [pyridine, imidazole and 1,8-bis(dimethylamino)naphthalene] are presented. Based on the dependence of the observed rate constants on the base concentration, kinetic schemes are proposed for the catalyzed decomposition of 1 and rate constants are assigned to specific reaction steps. The results obtained with the nitrogen bases give further support in favor of 1,2-dioxetane dione as the reactive intermediate in the peroxyoxalate reaction. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The peroxyoxalate system remains one of the most efficient chemiluminescent processes,[1,2] exhibiting luminescence quantum yields (Φ_{CL}) of up to 0.3 Einstein mol^{-1}. It consists of a base-catalyzed reaction between activated oxalic phenyl esters and hydrogen peroxide, in the presence of highly fluorescent aromatic hydrocarbons of low oxidation potentials (E_{ox}) as chemiluminescent activators (ACT). The excited-state generation in this system is believed to involve chemically initiated electron exchange luminescence (CIEEL),[3] a widely discussed mechanism for chemiluminescent peroxide decomposition.[4]

Recently, doubts about the efficiency of the CIEEL mechanism arose from a redetermination[5] of Φ_{CL} in the case of the diphenoyl peroxide decomposition (the prototypical CIEEL system), which proved to be three orders of magnitude lower than the previously reported[6] value. Although examples of highly efficient excited-state generation assumed to proceed by an intramolecular CIEEL-like mechanism have been reported,[7] the highly efficient peroxyoxalate system represents an ideal model for the study of the intermolecular CIEEL mechanism.

The mechanisms of the complex reaction between H_2O_2 and activated oxalic phenyl esters are still not well understood, especially with regard to the excitation step, the elementary step in which the electronically excited state of the activator is formed. Rauhut[1] postulated 1,2-dioxetane dione (**II**) as the high-energy intermediate responsible for ACT excitation. Other possible reactive intermediates (**I**, **III** and **IV**) have also been proposed in subsequent kinetic studies,[8–13] on the basis of indirect evidence.

Based on a kinetic study, we proposed a simplified scheme for the peroxyoxalate chemiluminescence. We concluded in favor of dioxetanedione (**II**) as the reactive intermediate structure, even though our suggestion was also supported only by indirect evidence.[14] Soon afterwards, we reported[15] the synthesis and characterization of a possible

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†This work is dedicated to the occasion of the 60th birthday of Professor Dr Waldemar Adam (Universität Würzburg, Germany).

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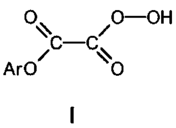

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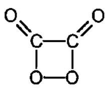

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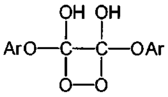

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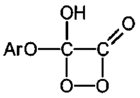


IV

intermediate of the peroxyoxalate chemiluminescence, namely 4-chlorophenyl *O,O*-hydrogen monoperoxyoxalate (**1**), a derivative of the peracid intermediate **I**. Here, we describe the results of a kinetic study of the chemiluminescence properties of the peracid derivative **1**, using various oxygen and nitrogen bases and in the presence of the commonly utilized chemiluminescence activator in the peroxyoxalate reaction, 9,10-diphenylanthracene (DPA).[14] The results permit us to rule out peracid derivatives of type **I** as reactive intermediates in the peroxyoxalate chemiluminescence. Furthermore, we present kinetic evidence for 1,2-dioxetanedione (**II**) as the key intermediate, which upon interaction with a chemiluminescence activator leads to the generation of the activator excited state and consequently to light emission.

RESULTS

The peracid **1** was prepared as described previously.[15] In the presence of DPA alone, **1** is stable and no chemiluminescence is observed.

Reaction of 1 with oxygen bases

In the presence of potassium hydroxide, potassium *tert*-butoxide (TB) or potassium *p*-chlorophenolate (CP) and DPA in THF, light emission corresponding to DPA fluorescence is obtained from **1** (Figure 1). At low base concentrations ([TB] < 2 mM, [CP] < 1 mM), slow decay curves, having low emission intensities, are obtained. However, at higher concentrations, a strong acceleration of the reaction is observed, accompanied by an increase in the emission intensity. The decay constants, although poorly reproducible, are independent of the base concentration ([TB] = 2·0–3·0 mM, $k_{\mathrm{obs}} = 0{\cdot}43 \pm 0{\cdot}10\ \mathrm{s}^{-1}$; [CP] = 1·0–2·0 mM; $k_{\mathrm{obs}} = 0{\cdot}25 \pm 0{\cdot}05\ \mathrm{s}^{-1}$).

The [base] threshold where the faster kinetics are observed depends on the batch of the stock solution of **1** used, indicating that this behavior may be due to trace amounts of water present in the stock solution, which cannot be completely removed without destruction of **1**. Indeed, the addition of water increases the base concentration necessary to obtain the fast kinetics.

Reaction of 1 with nitrogen bases

Treatment of **1** in the presence of DPA with pyridine ($\mathrm{p}K_a = 5{\cdot}25$) in ethyl acetate does not result in light emission or decomposition of the peracid. However, with imidazole (IMI) ($\mathrm{p}K_a = 6{\cdot}95$) or 1,8-bis(dimethylamino)naphthalene (BDN) ($\mathrm{p}K_a = 12{\cdot}34$) strong light emission accompanied by decomposition of **1** is observed (Figure 2). The observed decay rate constant is dependent on [IMI] (Table 1). At low concentrations ([IMI] ≤ 20 mM), a linear dependence is observed (Figure 3, inset) with a bimolecular rate constant $k_{1(2)} = 0{\cdot}96 \pm 0{\cdot}02\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. In the high concentration range ([IMI] = 100–250 mM), a second-order dependence on [IMI] is obtained ($k_{\mathrm{obs}} = k_{1(3)}\ [\mathrm{IMI}]^2$), leading to a termolecular rate constant $k_{1(3)} = 1{\cdot}6 \pm 0{\cdot}2\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. The kinetics are also observed by measuring the absorption change at 292 nm,

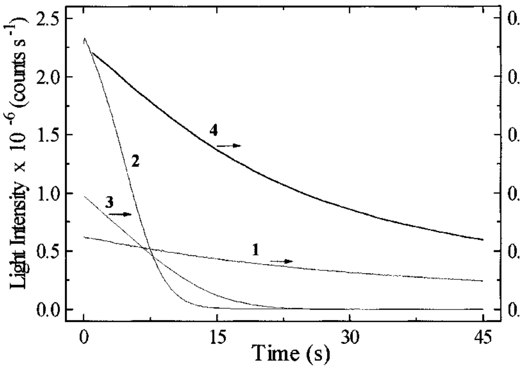


Figure 1. Chemiluminescent decomposition of **1** (0·50 mM), catalyzed by *tert*-butoxide and *p*-chlorophenolate, in the presence of DPA (1·0 mM) in THF. 1 -[TB] = 1·2 mM, 2-[TB] = 2·9 mM, 3-[CP] = 0·70 mM, 4-[CP] = 1·0 mM

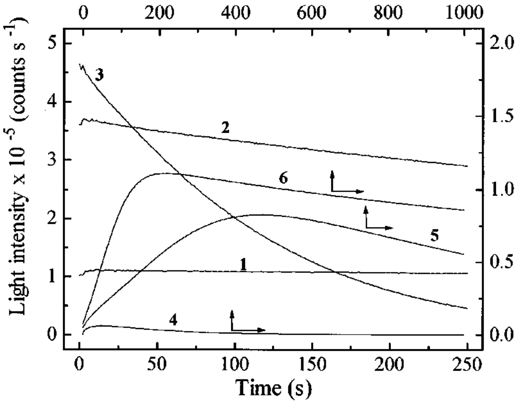


Figure 2. Chemiluminescent decomposition of **1** (0.50 mM), catalyzed by imidazole and 1,8-bis(dimethylamino) naphthalene, in the presence of DPA (1·0 mM) in ethyl acetate. 1, [IMI] = 0·10 mM; 2, [IMI] = 1·0 mM; 3, [IMI] = 10 mM; 4, [BDN] = 0·10 mM; 5, [BDN] = 0·50 mM; 6, [BDN] = 1·0 mM

Table 1. Dependence of the observed rate constants (k_{obs}) and the quantum yields (Φ) on the imidazole concentration for emission and absorption experiments[a]

No.	[IMI} (mM)	$k_{\mathrm{obs}} \times 10^3$ (s^{-1}) (emission)	$\Phi \times 10^4$ (E mol^{-1})	$k_{\mathrm{obs'}} \times 10^3$ (s^{-1}) (absorption)
1	0·10	0·34±0·2	46±7	0·18±0·04
2	0·40	0·53±0·1	51±2	–
3	0·50	–	–	0·63±0·01
4	0·60	0·72±0·1	41±7	–
5	0·80	0·88±0·1	38±7	–
6	1·0	1·1±0·3	35±2	3·5±0·1
7	2·0	2·1±0·2	20±1	–
8	4·0	3·9±0·2	11±0·6	–
9	4·6	–	–	7·6±0·4
10	6·0	5·7±0·2	7·8±0·1	–
11	8·0	7·6±0·7	6·2±0·02	10·0±0·2
12	10	10±1	5·1±0·1	–
13	11	–	–	14·6±0·3
14	13	–	–	19·0±0·3
15	20	16±1	3·1±0·1	25±2
16	30	25±5	2·3±0·06	27±2
17	40	30±5	1·7±0·05	30·9±0·2
18	50	37±6	1·3±0·08	36·2±0·3
19	60	41±4	1·2±0·02	41·1±0·4
20	70	47±6	1·0±0·03	–
21	80	50±2	0·91±0·05	53±1
22	100	59±1	0·80±0·03	51±1
23	125	72±3	0·70±0·04	–
24	150	83±2	0·52±0·01	–
25	175	98±4	0·56±0·06	–
26	200	115±2	0·50±0·08	–
27	250	155±9	0·38±0·03	–

[a] [**1**] = 0·50 mM, [DPA] = 1·0 mM, in ethyl acetate.

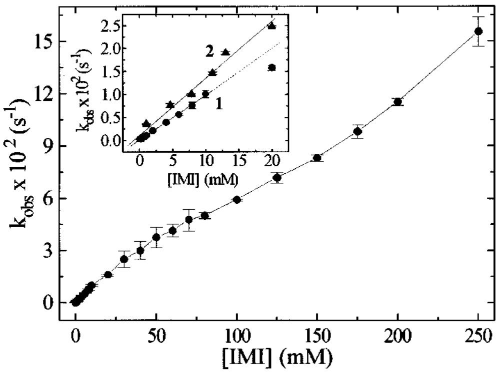


Figure 3. Dependence of the observed rate constants (k_{obs}) on the imidazole concentration for emission experiments. At [IMI] ⩾ 100 mM, the values were fitted using the equation $k_{\mathrm{obs}} = C + k_{1(3)}[\mathrm{IMI}]^2$, where $C = 0{\cdot}040 \pm 0{\cdot}005\ \mathrm{s}^{-1}$ and $k_{1(3)} = 1{\cdot}6 \pm 0{\cdot}2\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$. Inset: linear dependence in emission (1), $k_{1(2)} = 0{\cdot}96 \pm 0{\cdot}02\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ ($r = 0{\cdot}99$), and in absorption experiments (2), $k_{1(2)'} = 1{\cdot}24 \pm 0{\cdot}06\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ ($r = 0{\cdot}99$). [**1**] = 0·50 mM, [DPA] = 1·0 mM, in ethyl acetate

due to the release of *p*-chlorophenol (Table 1). From the linear dependence of $k_{\mathrm{obs'}}$ in the low concentration range (Figure 3, inset), a bimolecular rate constant of $k_{1(2)'}' = 1{\cdot}24 \pm 0{\cdot}06\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ is obtained, in reasonable agreement with the emission rate constant under these conditions. In the high concentration range ([IMI] > 100 mM), no reliable rate constants can be obtained in the absorption measurements, since the samples of **1** contain 4-chlorophenyl hydrogen oxalate (**2**), from which the release of *p*-chlorophenol is also observed at high [IMI]. Independent measurements confirmed, however, that **2** reacts at least 40 times slower than **1** with IMI at [IMI] < 100 mM. Therefore, the observed *p*-chlorophenol release in the low concentration range is exclusively due to the reaction of the peracid derivative **1**.

With BDN as base, emission curves going through an intensity maximum are observed (Figure 2), from which a decay rate constant k_{obs1} and a rise rate constant k_{obs2} can be obtained. Both rate constants show only a slight variation with [BDN] up to about 1 mM; at higher concentrations a linear dependence is obtained (Table 2, Figure 4). From the linear region, bimolecular rate constants $k_{1(2)} = 37 \pm 1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_{2(2)} = 140 \pm 20\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for the decay and the rise in light intensity, respectively, are obtained. The insensitivity of the rate constants to the base concentration at low [BDN] is assumed to be due to the presence of water in the stock solutions of **1** (see above). In agreement with this interpretation, the addition of water to the kinetic sample leads to an extension of the concentration-insensitive range, corresponding to the amount of water added.

We found that the quantum yields decrease with increasing [IMI] and [BDN] (Tables 1 and 2). In the case of BDN, this decrease is much less pronounced at higher [DPA] (Table 2, compare entry 2 with 10 and entry 2a with 10a). Similar results are obtained with IMI as catalyst (data not shown) and were also observed in our previous study on the reaction.[14] As IMI and BDN do not quench the DPA fluorescence emission at concentrations up to 0.1 M (data not shown), these facts indicate an interaction between the bases and the reactive intermediate, in competition with its interaction with DPA, which leads to excited-state formation.

Finally, it is important to point out that the rate constants obtained with the different bases are independent of the activator concentration under all experimental conditions.

DISCUSSION

Primarily, our results indicate that the peracid derivative **1** does not interact directly with the chemiluminescence activator DPA. It should be mentioned that also on using activators with lower oxidation potentials (e.g. rubrene, perylene, pyrene), which should be more reactive according to the CIEEL mechanism, no direct interaction of **1** with these activators is observed.[16] The observation of light emission and decomposition of **1** in the presence of the

Table 2. Dependence of the fall rate constants (k_{obs1}), the rise rate constants (k_{obs2}) and the quantum yields (Φ) on the 1,8-bis(dimethylamino)naphthalene concentration[a]

No.	[BDN] (mM)	$k_{obs1} \times 10^3$ (s^{-1})	$k_{obs2} \times 10^2$ (s^{-1})	t_{max} (s)	$I_{max} \times 10^{-3}$ (counts s^{-1})	$\Phi \times 10^5$ (E mol^{-1})
1	0·10	0·40 ± 0·03	1·2 ± 0·2	283	109	212
2	0·20	0·57 ± 0·03	1·6 ± 0·8	320	147	213
2a[b]	0·20	0·55 ± 0·01	2·1 ± 0·2	300	219	277
3	0·30	1·2 ± 0·1	0·49 ± 0·06	428	123	117
4	0·40	1·4 ± 0·1	0·32 ± 0·01	479	93	83
5	0·50	1·2 ± 0·1	0·35 ± 0·02	483	79	76
6	0·60	1·9 ± 0·4	0·27 ± 0·02	463	38	35
7	0·70	4·0 ± 0·1	0·47 ± 0·02	165	12	5·0
8	0·80	5·0 ± 0·1	5·0 ± 0·1	51	8·9	1·49
9	0·90	8·1 ± 0·1	7·1 ± 0·1	34	7·3	0·81
10	1·0	12 ± 2	8·3 ± 0·1	30	6·1	0·53
10a[b]	1·0	15 ± 2	10 ± 2	25	52	33
11	1·5	27 ± 2	12 ± 1	16	3·9	0·15
12	2·0	48 ± 3	18 ± 1	10	2·9	0·068
13	2·5	54 ± 5	31 ± 1	9	0·24	0·043
14	3·0	83 ± 5	–	–	–	–
15	3·5	91 ± 5	–	–	–	–
16	4·0	113 ± 8	–	–	–	–
17	4·5	140 ± 9	–	–	–	–
18	5·0	165 ± 9	–	–	–	–

[a] [**1**] = 1·3 mM, [DPA] = 1·0 mM, in ethyl acetate.

[b] [DPA] = 10 mM.

oxygen bases indicates that the deprotonation of the peracid is necessary and sufficient to initiate the reaction forming the reactive intermediate able to generate excited states upon its interaction with the activator. However, the quantum yields are considerably lower with these bases than with imidazole as catalyst (about two orders of magnitude; results not shown) and the decay kinetics are much faster. This may be due to a nucleophilic attack of bases such as hydroxide or *tert*-butoxide on the ester carbonyl carbon, leading to a non-chemiluminescent transformation of the peracid **1** (Scheme 1). Although the reproducibility of the results with these bases is poor, the decay constant at high [CP] of around 0·25 s^{-1} can be considered as an estimate of the rate constant of the transformation of the peracid anion to the reactive intermediate. The fact that the rate constant obtained with TB is higher than that observed with CP indicates the predominance of the nucleophilic attack of TB to the ester carbon.

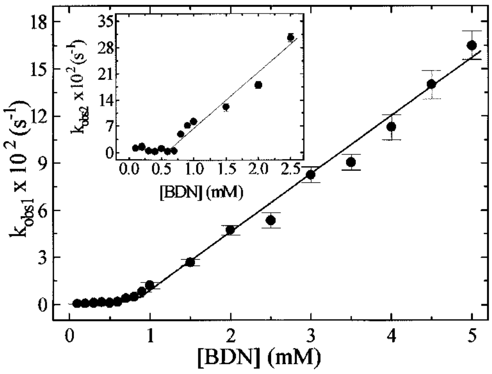
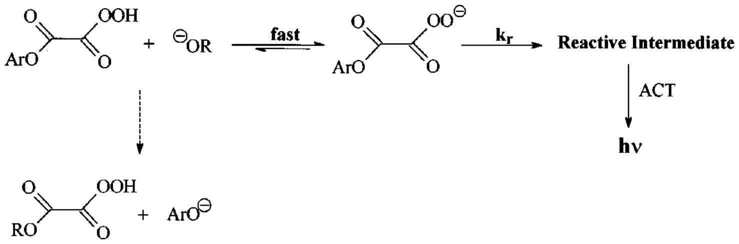


Figure 4. Dependence of the fall (k_{obs1}) and rise (k_{obs2}, inset) rate constants on the BDN concentration. $k_{1(2)} = 37 \pm 1$ M^{-1} s^{-1} ($r = 0·99$) and $k_{2(2)} = 140 \pm 20$ M^{-1} s^{-1} ($r = 0·98$). [**1**] = 1·3 mM, [DPA] = 1·0 mM, in ethyl acetate

The complex dependence of the decay rate constant on the [IMI] can be rationalized on the basis of Scheme 2. The linear dependence at low [IMI] reflects the deprotonation equilibrium of **1** and the bimolecular rate constant ($k_{1(2)} \simeq 1·0$ M^{-1} s^{-1}) is composed of k_r and the pK_a values of IMI and the peracid **1**. These pK_a values are not known in ethyl acetate, the solvent used, and therefore we ought not try to estimate values of k_r under these conditions. Furthermore, the reaction may also be catalyzed by IMI (general acid catalysis of the extrusion of the phenolate). The second-order dependence at high [IMI] is due to the nucleophilic imidazole attack, catalyzed by imidazole, on the phenyl ester moiety.[17] This behavior is similar to that observed in a kinetic study of bis(2,4,6-trichlorophenyl) oxalate (TCPO) with hydrogen peroxide catalyzed by imidazole.[14] However, the termolecular rate constant obtained in the reaction of **1** [$k_{1(3)} = 1·6$ M^{-2} s^{-1}] is two orders of magnitude lower than that obtained for the same reaction step with TCPO under similar conditions. This difference reflects the deactivation of the ester carbonyl



Scheme 1. Chemiluminescent and non-chemiluminescent decomposition of the peracid **1** in the presence of DPA, catalyzed by oxygen bases (R = H, *tert*-butyl and *p*-chlorophenyl)

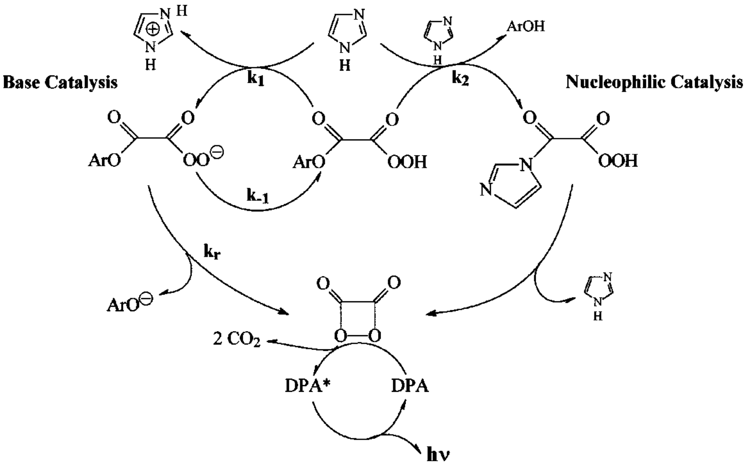
group towards nucleophilic attack by the adjacent peracid moiety as compared with the corresponding diester.[11,18] Additionally, the trichlorophenyl substituent in TCPO may contribute to the increased reactivity. Interestingly, the IMI dependence of the TCPO reaction does not show the linear region observed in our present study on **1**. Of course, in the former system, the possibility of a proton abstraction from the substrate does not exist. Therefore, this comparison contributes to confirmation of the validity of Scheme 2.

The kinetic constants obtained at low [IMI] are attributed to the cyclization of the peracid anion to 1,2-dioxetane dione (**II**), as the cyclization reaction appears to be the only 'reasonable' chemical transformation possible in this system.

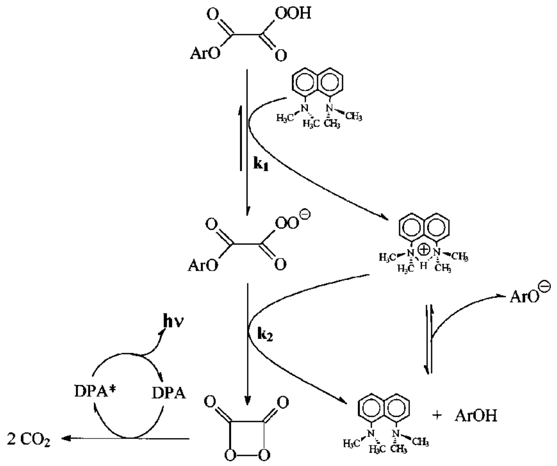
An alternative pathway may be the interaction of the anion of **1** with protonated **1** leading to a type of peranhydride. However, if this reaction were an important pathway for light emission, the observed rate constants as well as the quantum yields (Φ) should depend on the initial concentration of **1**. The experimental observation that both k_{obs} and Φ do not depend on the concentration of **1** indicates that the above-mentioned possibility is surely of minor importance in the chemiluminescent pathway. Furthermore, the hypothetical peranhydride structure is not supposed to contain sufficient energy for excited-state generation upon interaction with the activator.

The other cyclic peroxide, which may be obtained by the cyclization of the anion of **1**, the 1,2-dioxetanone derivative **IV**, appears to be a less likely candidate for the reactive intermediate structure for reasons discussed earlier[14] (see also below). The same cyclization step should be involved at high [IMI], but in this case the much better leaving group imidazole is replaced and this step is not observed kinetically.

The kinetic results obtained on using BDN as the base catalyst can be rationalized on the basis of Scheme 3. The decay constant k_{obs1}, which depends linearly on [BDN], corresponds to the slow proton transfer from the peracid **1** to the strong and extremely hindered base. The value for the bimolecular rate constant [$k_{1(2)} = 37\ \text{M}^{-1}\,\text{s}^{-1}$] is of the same magnitude as that obtained for the proton transfer from water to this base ($k_{H2O} \simeq 70\ \text{M}^{-1}\,\text{s}^{-1}$).[19] The observation of a slow rise in the kinetic curves with BDN is surprising when compared with the kinetic curves obtained with IMI, where the onset of luminescence is so fast that only its decay is observed. Moreover, k_{obs2} shows a linear dependence on the [BDN]. This constant is assigned to the cyclization of the peracid anion, occuring with the concomitant release of the phenolate—a reaction susceptible to general acid catalysis by the corresponding acid of BDN. In turn, the observed



Scheme 2. Base and nucleophilic catalysis in the imidazole-catalyzed chemiluminescent decomposition of **1** in the presence of DPA



Scheme 3. Chemiluminescent decomposition of **1**, in the presence of DPA, catalyzed by 1,8-bis(dimethylamino)naphthalene

catalysis of the cyclization step by BDN allows the conclusion that this step is accompanied by the release of the phenolate, a fact which excludes the 1,2-dioxetanone structure **IV** as a reactive intermediate and adds an additional piece of evidence in favor of 1,2-dioxetanedione (**II**) as the reactive intermediate in the peroxyoxalate reaction. Alternatively, the cyclization could be a fast process and the release of the phenolate from the tetrahedral intermediate the kinetically observed step. However, as the rate constants do not depend on the activator concentration, also in this case, the phenolate release would precede the interaction of the reactive intermediate with the activator. Therefore, the reactive intermediate does not contain the phenolic substituent and the most probable structure for this compound is 1,2-dioxetanedione (**II**).

Finally, it must be pointed out that the results obtained with IMI and BDN cannot be quantitatively compared, because the rate constants in the two cases are related to different events. Furthermore, it should be mentioned that the quantum yields obtained from the reaction of **1** with IMI in the presence of DPA (Table 1) are at least 10 times lower than that reported for the peroxyoxalate reaction with TCPO, in presence of the same activator, also catalyzed by IMI under almost identical experimental conditions.[14] This difference is considered to be caused by the low stability of the peracid **1** and may also be due to the impurities present in the sample of **1**.[15] In the reaction catalyzed by BDN, the still lower quantum yields (Table 2) are probably caused by a more efficient interaction of BDN with the reactive intermediate (see above).

CONCLUSIONS

The results from our kinetic study on the chemiluminescence properties of the peracid derivative **1** clearly rule out this type of compound as reactive intermediate in the peroxyoxalate reaction as it does not interact directly with the activator. However, in the presence of any of several bases and an activator, chemiluminescence emission and decomposition of **1** are observed. The results with oxygen bases show that a simple deprotonation of the peracid initiates the chemiluminescence pathway (Scheme 1). With nitrogen bases, it can first be shown that a base with a pK_a of at least 6 is necessary, since pyridine (pK_a=5·25) is not able to elicit light emission from **1**. With IMI as catalyst, two distinct processes are involved. IMI at low concentration acts mainly as a base catalyst and the kinetically observed step is the cyclization of the peracid anion. At high [IMI] the prominent process is nucleophilic catalysis and the observed decay constant reflects the IMI-catalyzed attack of IMI on the ester function of **1**, leading to an imidazole-substituted peracid derivative, which in turn suffers fast base-catalyzed cyclization (Scheme 2). On the other hand, with BDN a rise and a decay constant are observed, both depending on the [BDN] in a linear fashion. The decay constant corresponds to the deprotonation step, which is slow in the case of this strong but extremely hindered base. The rise constant is related to the cyclization and concomitant *p*-chlorophenol release, which shows general acid catalysis by the corresponding acid of BDN (Scheme 3).

The kinetic results, especially those obtained with BDN, can best be rationalized by the formation of 1,2-dioxetanedione as the reactive intermediate. The interaction of this cyclic peroxide with the activator, which leads ultimately to the generation of the activators excited state, cannot be observed kinetically, as the observed rate constants are independent of the ACT concentration under all experimental conditions.

EXPERIMENTAL

Reagents. Imidazole (99%, Aldrich), *p*-chlorophenol (99%, Merck) and 1,8-bis(dimethylamino)naphthalene were used as received. Pyridine (99%, Aldrich) was refluxed for 4 h over NaOH and then distilled. Ethanol (99%) and *tert*-butanol were distilled over sodium wire (7 g per 100 ml). 4-Chlorophenyl *O,O*-hydrogen monoperoxyoxalate (**1**) was prepared according to the literature procedure.[15] Ethyl acetate was dried for 1 day over $CaCl_2$, stirred for 30 min over NaOH (pellets, 40 g l^{-1}) at 0°C, distilled after filtration, kept for 1 day over 4 Å molecular sieves, carefully distilled through a 30 cm Vigreux column under a nitrogen atmosphere (b.p. 77°C) and stored over freshly dehydrated 4 °A molecular sieves under nitrogen. THF was refluxed for 4 h with sodium wire and benzophenone and distilled immediately before use. A TB stock solution in THF was prepared by addition of 9·8 ml (0·10 mol) of *tert*-butanol to a stirred suspension of 4·0 g (0·10 mol) of potassium in THF under a dry nitrogen atmosphere. The mixture was refluxed for 4 h and the TB concentration determined by titration with HCl using phenolphthalein as indicator. CP was prepared by addition of 3·9 g (30 mmol) of *p*-chlorophenol in 10 ml of ethanol to 1·7 g (30 mmol) of KOH in 50 ml of ethanol with stirring under a dry nitrogen atmosphere. The solvent was evaporated and the solid dried in vacuum. The CP stock solution was prepared by dissolving the solid obtained in THF and its concentration was determined by titration with HCl using phenolphthalein as indicator.

Apparatus. Chemiluminescence measurements were performed on a SPEX-Fluorolog 1681 spectrofluorimeter (slit, 1·0 mm, grates on mirror position; photomultiplier voltage, 750 kV). For the quantum yield determinations, the instrument was calibrated by using luminol standard.[20] Absorption measurements were carried out on a HITACHI U-2000 spectrophotometer.

Kinetics experiments. All kinetic measurements were carried out in quartz fluorescence or absorption cuvettes (10 × 10 mm; final volume 3.0 ml) at 25·±0·2°C. The experiments with TB and CP were initiated by fast addition of a stock solution of **1** (7·5 μl, 200 mM, determined iodimetrically[21]) in THF, immediately followed by the appropriate amount of the TB (0·80 M) or CP (0·50 M) stock solutions in THF, to a stirred solution of DPA in THF (final concentrations: [**1**] = 0·50 mM, [DPA] = 1·0 mM, [TB] = 1·0–3·0 mM, [CP] = 0·10–2·0 mM). The chemiluminescence measurements with IMI and BDN were initiated by fast addition of an ethyl acetate stock solution of **1** (7·5 or 15 μl, 200 mM) to a stirred solution of DPA and IMI or BDN in ethyl acetate (final concentrations: [**1**] = 0·50 or 1·0 mM, [DPA] = 1·0 mM, [IMI] = 0·1–250 mM, [BDN] = 0·1–5·0 mM). The absorption experiments with IMI were performed in the same way but in the absence of DPA.

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