Table IV. Treatment of Deuterio-2 with the Catalyst. Isotopic Compositions of Reactant and Recovered Deuterio-2

	% composition[a]							
	reactant **2**				recovered 2			
run	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3
1	0.9	4.9	26.0	67.9	0.9	5.6	27.5	66
2	0.1	4.0	26.8	69.0	0.1	3.8	25.4	70.7
3	0.1	4.0	26.8	69.0	1.0	3.9	21.9	73.2

[a] Determined by mass spectrometry.

nitrogen. The third trap was then connected to a GLC loop, cooled with liquid nitrogen, which was in turn connected to two 20-ft β,β'-oxydipropionitrile on firebrick GLC columns and the products were separated at 0 °C. The decarbonylation products were then analyzed by ^1H and ^2H NMR and mass spectrometry.

Isolation of Ethylene and Ethylene-*d*. A deoxygenated solution of 0.10 mL (0.90 mmol) of 4-hexenal-*1-d* (87% trans) and 0.060 mL of toluene standard in 1.4 mL of benzene was added to 0.084 g (0.090 mmol) of **1**. The mixture was stirred under argon at room temperature for several minutes, cooled to -198 °C, and evacuated. One millimole of C_2H_4 (25 mL at 1 atm) was then transfered to the reaction flask, which was then sealed. The resulting mixture was warmed to room temperature and stirred for 48 h, after which the volatiles were removed in vacuo, the ethylene was collected in a liquid nitrogen cooled trap, and the other volatiles were collected at -78 °C in a trap that preceded it. The ethylene was analyzed by mass spectrometry.

Treatment of 2-*2,5,5*-d_3[35] with the Catalyst. Following the usual procedure, a sample composed primarily of **2**-*2,5,5*-d_3 was treated with **1** (ketone:**1** = 10) in C_6H_6 at 25 °C for 24 h. The isotopic compositions of the ketone reactant and of recovered deuterio-**2** are given in Table IV (run 1).

The data for runs 2 and 3 in Table IV derive from experiments in which 4-pentenal was treated with **1** in C_6H_6 in the presence of deuterio-**2** (4-pentenal:ketone:**1** = 10:1.5:1.0). During 6 h at 25 °C, 46% of the 4-pentenal was converted to cyclopentanone in 41% yield. Recovered 4-pentenal and the cyclopentanone possessed >99% d_0 compositions. No 4-hexenal was detected in the product mixtures. The 90-MHz ^1H NMR spectra of the ketone reactant and product in run 3, recorded in the presence of Eu(fod)$_3$ shift reagent, were integrated. They showed an average of 0.31 and 0.34 H, respectively, at C-2 + C-5 in the deuterio-**2** starting material and in the recovered deuterio-**2**. The isotopic compositions for run 3, Table IV, showed values of 0.35 and 0.34 H for reactant **2** and recovered **2**, respectively.

Synthesis of 2-Methylcyclopentanone-*2,3-d*$_2$. In a typical experiment, a solution of 0.10 mL (0.98 mmol) of 2-methylcyclopent-2-en-1-one[37] in 5 mL of deoxygenated benzene was added to 0.109 g (0.118 mmol) of **1** under argon. The flask was cooled to -78 °C and then attached to a hydrogenation apparatus. An atmosphere of D_2 was introduced; then the reaction mixture was allowed to warm to room temperature. The reaction was monitored by following the rate of consumption of D_2 and by GLC analysis of 5-μL aliquots which were removed periodically. The reaction was terminated after the desired time by removal of all volatiles from the catalyst in vacuo. The deuterio-**2** was then collected via GLC after removal of solvent.

Synthesis of 2-Methylcyclopentanone-*3-d* Diastereomers. To a flask containing 0.7 mL of 20% hydrochloric acid and 0.8 mL of methanol was added *cis*-2,3-dideuterio-2-methylcyclopentanone (0.15 mL 1.4 mmol). The mixture was stirred for ca. 16 h, after which the solution was saturated with NaCl and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the mixture of **2**-*3-d* isomers, 63% yield, was collected via GLC.

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Role of a Peroxide Intermediate in the Chemiluminescence of Luminol. A Mechanistic Study

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Abstract: By simultaneous generation of the luminol radical and the superoxide radical anion $O_2^{-\cdot}$ in an alkaline aqueous solution containing H_2O_2 but no oxygen, it was possible to measure at different pH values the rate constant for the formation of the peroxide adduct. The rate constant for the decomposition of the adduct was also determined. The latter reaction is shown to be a rate-determing kinetic step in the production of the excited state. Its rate constant is strongly pH dependent. At pH 7.7, where essentially no light is produced, its value is $(2 \pm 0.5) \times 10^3$ s^{-1}, while at pH 11.0 the value $(1.8 \pm 0.3) \times 10^5$ s^{-1} is obtained. It is suggested that the acid (hydroperoxide) and the base (peroxide) react along different chemical pathways yielding different end products. Only the decomposition of the base results in light generation. An overall reaction scheme is proposed. In an indirect measurement the chemiluminescence quantum yield ϕ_{cl} is determined to be $\simeq$0.1.

Introduction

Ever since the discovery of the chemiluminescence of luminol by Albrecht,[1] many chemists have been intrigued by the elusive nature of the light-producing step. A common feature endemic to all systems where luminol chemiluminescence is observed is the presence of oxygen or hydrogen peroxide and a basic environment. Thanks to the pioneering works of White et al.,[2,3] the stoichiometry of the overall reaction as well as the identity of the emitting species has been firmly established in aprotic solvents. By implication it appears reasonably safe to assume that the same species (3-aminophthalate) is the light emitter even in protic solvents, such as water.

A generally made observation is that the addition of hydrogen peroxide to an otherwise aerated solution enhances the chemiluminescent intensity. The mechanism of luminol chemiluminescence in aqueous solutions in the presence of oxygen (O_2) has been studied by Shevlin et al.[4] and by Baxendale.[5] These workers conclude that the chemiluminescent process is initiated by a

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one-electron oxidation of luminol followed by rapid addition of oxygen. Furthermore, both studies reveal the necessity of adding a second electron to the peroxy radical thus formed in order to prepare it for the final light-producing step.

Rauhut et al.[6] conclude from their studies on persulfate-initiated luminol chemiluminescence in aqueous hydrogen peroxide solutions that no radical mechanism is involved. They postulate the direct formation of 3-aminoazadione which subsequently reacts with hydrogen peroxide to yield light.

The present state of the art of luminol research is well concluded in the latest review by Roswell and White:[7] "In summary it appears that the luminol dianion is involved in aprotic oxidations, the radical anion in protic ones and the azaquinones very probably are involved in the light pathway."

In most "chemical" investigations, the initial oxidation of luminol by the added cooxidant is the rate-determining step. Consequently, no direct measurement can be made on the subsequent reactions. To circumvent this difficulty, we have employed the technique of pulse radiolysis on the system luminol–hydrogen peroxide in water in the absence of oxygen (O_2).

Experimental Section

The microtron accelerator[8] has a maximum pulse current of 200 mA and the pulse width is variable between 5×10^{-8} and 4×10^{-6} s. The dose/pulse is measured with a secondary emission chamber which is previously calibrated with an aerated aqueous 10^{-2} M KSCN solution taking $G\epsilon_{(SCN)_2^-} = 2.14 \times 10^4$ at 500 nm.[9] The reproducibility of the dosimeter is 2.5%. A bandwidth of 2.5 nm was used in all absorbance measurements. In chemiluminescence measurements the slits were removed from the monochromator. The computerized transient detection system with a time resolution of $\simeq 10^{-7}$ s is described elsewhere.[10] In solutions containing H_2O_2, $G_{OH\cdot} = 6.1$ was used in all calculations. The concentration of solute (0 luminol, H_2O_2) was kept sufficiently high to annihilate all OH· radicals in a single kinetic step. Unless otherwise specified all solutions were degassed by purging with Ar immediately before irradiation. Complete removal of oxygen in the degassing step was evidenced by the absence of chemiluminescence.

Luminol (p.a., 97%, Egachemie, ϵ_{310} 6000, ϵ_{355} 6600 in 0.1 N NaOH, H_2O), $Na_2B_4O_7 \cdot 10H_2O$, $Na_2HPO_4 \cdot 2H_2O$, H_2O_2 (all p.a. Merck), NaOH (p.a. EKA), and Ar (AGA, <5 ppm O_2) were used without further purification. Further purification of luminol did not change the integrated light intensity.

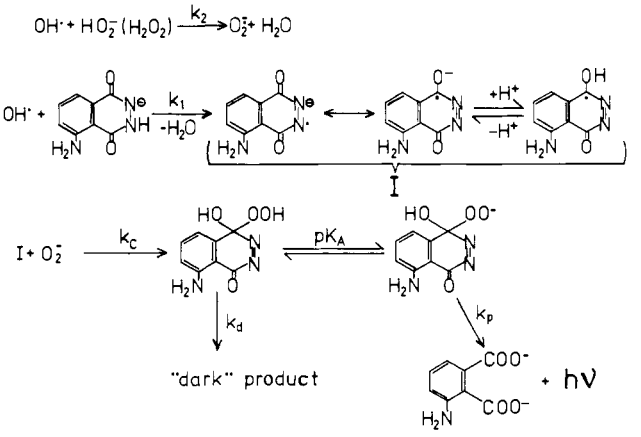
All solutions were prepared from water which was doubly distilled in quartz. To minimize decomposition of luminol and H_2O_2 in the solutions to be irradiated, the former were introduced into the buffer solutions just before degassing. In all runs 0.1 M buffer solutions were used unless otherwise stated; pH was adjusted by titration with 1 M NaOH. Control experiments at pH 9.3 showed that variation of the borate buffer concentration from 4×10^{-1} to 10^{-3} M had no effect on the integrated light intensity or the kinetics.

Results and Discussion

When ionizing radiation (γ rays, fast electrons, etc.) passes through liquid water, a rapid sequence of primary physical events occurs. Ultimately, the short-lived radical species OH·, e^-(aq), and H· are formed. At high pH in the presence of N_2O or H_2O_2 all radicals (i.e., e^-(aq) and H·) are converted into OH· radicals.[11] It is well known that OH· is one of the strongest oxidizing agents having a redox potential of +2.8 V.[12] Therefore, it is capable of oxidizing both luminol and H_2O_2.

Competition of Luminol and H_2O_2 for the OH· Radical. In a solution containing both luminol (at all pH values used in this work luminol is present in the form of its monoanion) and H_2O_2 these compounds compete for the OH· radicals to form luminol radicals and HO_2·, respectively. The latter immediately dissociates into the superoxide radical O_2^-· at high pH values ($pK_a = 4.8$).[13] The rate constant between OH· and H_2O_2 has been determined.[14] The rate constant increases monotonously with pH, as a result of dissociation of H_2O_2 into HO_2^-. Baxendale[5] has determined the rate constant for the reaction between luminol and OH· to be 8.7×10^9 M^{-1} s^{-1} (see Scheme I). The competition between luminol and H_2O_2 for OH· radicals can be studied by measuring the initial absorbance of the luminol radical as a function of the ratio between H_2O_2 and luminol. Such competition kinetic experiments were carried out at pH 7.7, 9.3, and 11.0, and by using the k_1 value of Baxendale the following rate constants, which are in good agreement with the literature values,[14] were found.

Scheme I



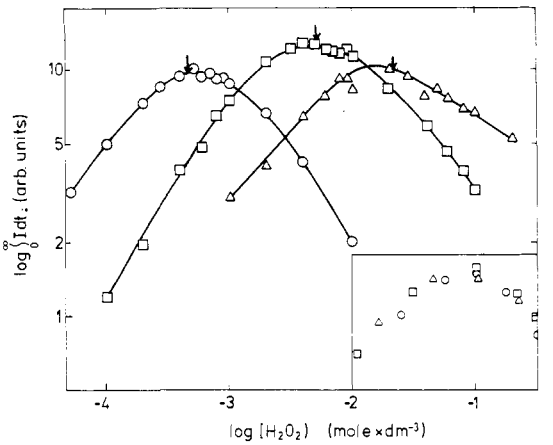


Figure 1. The integrated light intensity at pH 11.0 as a function of added H_2O_2 at three luminol concentrations, lum (○) 7.1×10^{-5}, (□) 8.4×10^{-4}, (△) 3.8×10^{-3} M. The insert is a plot in au of log $\int_0^\infty I\,dt$ vs. log ($[H_2O_2]/[lum]$).

$$OH\cdot + H_2O_2 \xrightarrow{k_2'} O_2^-\cdot + H_3O^+ \qquad k_2' = 3.7 \times 10^7\ M^{-1}\ s^{-1}$$

$$OH\cdot + HO_2^- \xrightarrow{k_2''} O_2^-\cdot + H_2O \qquad k_2'' = 6.7 \times 10^9\ M^{-1}\ s^{-1}$$

The experimentally measured rate constant k_2 is related to k_2' and k_2'' by the equation

$$k_2 = \frac{k_2'[H^+] + k_2''K_{H_2O_2}}{[H^+] + K_{H_2O_2}} \qquad (1)$$

where the dissociation constant of H_2O_2 $K_{H_2O_2} = 10^{-11.65}$.

Role of the Superoxide Anion O_2^-. In the present work rigorously deaerated solutions were studied. The absence of oxygen was evidenced by the absence of chemiluminescence when no hydrogen peroxide was added. Thus the question arose which species would activate the luminol radical for chemiluminescence.

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Table I. Rate Constants for the Recombination of the Luminol Radical (H_2O_2 5.0×10^{-4} M, Luminol 10^{-3} M)

pH	λ, nm	ε, cm M^{-1}	$2k \times 10^{-8}$, s^{-1} M^{-1}	dose, krad
7.7	430	2138	7.7	5.9
7.7	430	2100	8.3	5.0
7.7	430	2143	8.2	5.3
7.7	400	2610	8.1	5.4
7.7	450	1735	8.2	7.4
7.7	600	650	7.5	7.4
9.3	400	2320	6.2	4.8
9.3	600	420	6.7	6.7
11.0	400	2540	5.0	8.1
11.0	430	2074	4.7	6.3

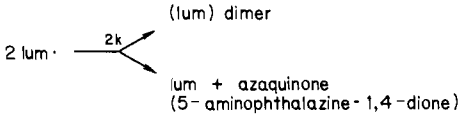
To investigate this, the integrated chemiluminescent intensity as a function of H_2O_2 at three different luminol concentrations was measured. Figure 1 shows conclusively that at a given dose the absolute concentrations of luminol and H_2O_2 are immaterial provided that they are in excess of produced OH·. Only their ratio will determine the total light yield (see insert, Figure 1). Thus, within the limits of the experimental accuracy the maximum light obtainable is unchanged, though H_2O_2 is varied by more than a factor of 50. We conclude that the activating species is not H_2O_2 but the superoxide radical anion $O_2^{-}\cdot$. Therefore, the first step on the path toward the excited state is a rapid addition of $O_2^{-}\cdot$ to the luminol radical to form a nonradical peroxide adduct.

Let us consider a solution where a certain amount of luminol radicals and $O_2^{-}\cdot$ have formed. The dismutation of $O_2^{-}\cdot$[14] into H_2O_2 and O_2 is rather slow at the pH values chosen. In an experiment performed on a solution containing 10^{-4} M luminol and 10^{-1} M H_2O_2 at pH 11 where only $O_2^{-}\cdot$ is formed, the half-life of the $O_2^{-}\cdot$ radical was estimated to be 40 ms as monitored by its absorbance at 260 nm. Thus on the time scale of all the other experiments presented in this paper the only channel in which $O_2^{-}\cdot$ can be consumed is its reaction with the luminol radical. However, lum· can both react with $O_2^{-}\cdot$ and recombine with itself. Since only the reaction between lum· and $O_2^{-}\cdot$ will lead to chemiluminescence, the following relationship is obtained.

$$\int_0^\infty I\,dt \propto \frac{\int_0^\infty k_c[\text{lum}\cdot][O_2^{-}\cdot]dt}{\int_0^\infty (k_c[\text{lum}\cdot][O_2^{-}\cdot] + 2k[\text{lum}\cdot]^2)\,dt} \qquad (2)$$

I denotes the chemiluminescent intensity; k_c and $2k$ denote the rate constants of lum· toward $O_2^{-}\cdot$ and lum·, respectively. The task at hand will be to maximize the light integral with respect to the ratio of $[\text{lum}\cdot]_0$ and $[O_2^{-}\cdot]_0$ initially formed. It can be shown that the integral is a rather insensitive function of $k_c/2k$. It has a maximum at $[\text{lum}\cdot]_0/[O_2^{-}\cdot]_0 = 1$, when $k_c = 2k$, and deviates only slightly from 1 as long as $2k$ and k_c are of the same order of magnitude. Tables I and II show that this is actually the case. By use of the rate constants k_1 and k_2 (the latter from eq 1) the concentrations of H_2O_2 were calculated where equal amounts of lum· and $O_2^{-}\cdot$ are formed. These concentrations are marked by arrows in Figure 1. As seen these calculated concentrations coincide well with those at which the light integrals obtain their maxima. The same satisfactory agreement was also obtained at pH 9.2 and 8.4.

Determination of $2k$. Figure 2 shows the transient spectra as obtained by pulse radiolysis of an aqueous solution of luminol at pH 7.7. The H_2O_2 concentration is kept sufficiently high to convert all radicals into OH·, but low enough not to produce appreciable amounts of $O_2^{-}\cdot$. At the end of the electron pulse the spectrum is that of the luminol radical distorted by the bleaching of the parent luminol below 390 nm. The structure of the luminol radical is not unambiguously determined. However, the fact that other substituted hydrazides yield radicals with similar wavelength maxima in their spectra[15] leaves little doubt that the unpaired electron is mainly located on the heteroring. In this experiment the only pathway whereby lum· can disappear is by recombination. This could proceed in two ways.



The azaquinone of luminol has an absorption band between 450 and 750 nm with $\epsilon_{550} \simeq 2700$ cm M^{-1}.[16] Thus from the final absorption spectrum in Figure 2 it is concluded that dimerization accounts for at least 80% of the recombination total.

Table I summarizes the ε values for the luminol radical and presents the rate constant for recombination. The decrease of the rate constant of recombination with increasing pH suggests dissociation of the luminol radical somewhere between pH 8 and 11.

Determination of k. In order to determine the rate constant for the reaction

$$\text{lum}\cdot + O_2^{-}\cdot \xrightarrow{k_c} (\text{lum}O_2)^{-} \qquad (3)$$

transient spectra in the presence of a large excess of H_2O_2 were

Table II. Rate Constants for the Reaction between the Luminol Radical and $O_2^{-}\cdot$

pH	$k_c \times 10^{-8}$, M^{-1}, s^{-1}	dose, krad	$c_{H_2O_2}$, M	c_{lum}, M	method
7.7	12.6	3.7	10^{-1}	9×10^{-5}	Adk[a] at 450 nm
7.7	13.7	3.8	10^{-1}	9×10^{-5}	Adk at 430 nm
7.7	15.6	3.8	10^{-1}	9×10^{-5}	Adk at 400 nm
9.3	9.1	6.5	1.0	10^{-3}	Adk at 430 nm
9.3	9.9	13.6	1.0	10^{-3}	Adk at 430 nm
9.3	10.0	6.3	1.0	10^{-3}	Adk at 500 nm
9.3	8.2	13.5	1.0	10^{-3}	Adk at 500 nm
9.3	8.3	16.8	1.0	10^{-3}	Chbk[b]
11.0	1.6	4.5	10^{-1}	10^{-3}	Chdk[c]
11.0	2.3	1.9	10^{-1}	10^{-3}	Chdk
11.0	2.3	9.4	10^{-1}	10^{-3}	Chdk
11.0	1.9	8.1	10^{-1}	10^{-3}	Adk at 430 nm
11.0	2.2	4.5	10^{-1}	10^{-3}	Adk at 430 nm

[a] Adk = absorbance decay kinetics. [b] Chbk = chemiluminescence buildup kinetics. [c] Chdk = chemiluminescence decay kinetics.

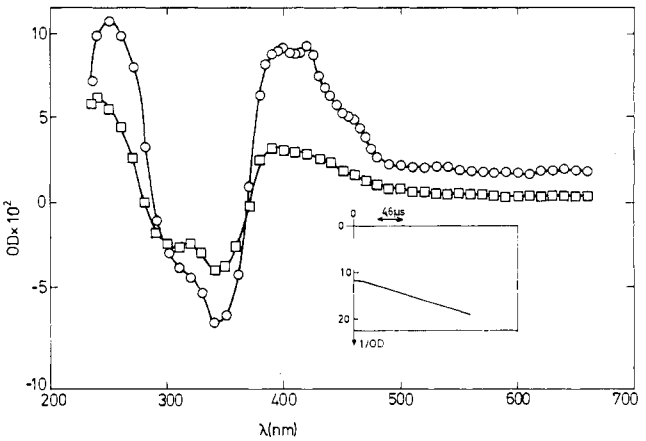


Figure 2. Transient absorption spectra of an aqueous solution containing 10^{-3} M luminol and 10^{-3} M H_2O_2 at two different times: (○) at the end of the electron pulse and (□) 210 μs later. The inset shows a second-order kinetic plot of the experimental data at 400 nm and a dose equal to 6.1 krad, pH 7.7.

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(16) (a) J. Lind, G. Merényi, and T. E. Eriksen, to be published. (b) The spectrum of naphthophthalazine-1,4-dione with a broad absorbance centered around 530 nm has been reported: K. D. Gundermann in "Chemiluminescence and Bioluminescence", Plenum Press, New York, 1973, p 209.

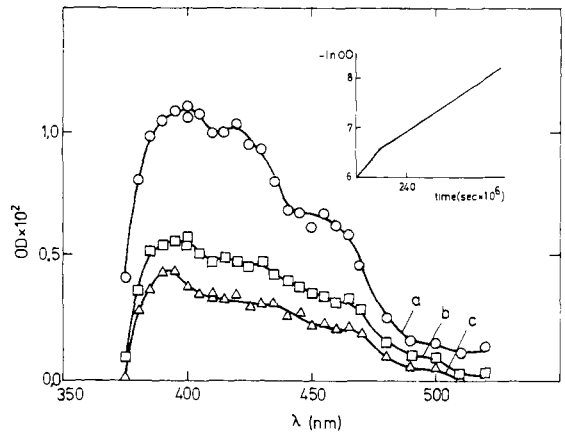

Figure 3. Transient absorption spectra of an aqueous solution containing 10^{-4} M luminol and 3×10^{-2} M H_2O_2 at pH 9.3: (a) 27, (b) 175, and (c) 650 μs after the end of the electron pulse. The inset shows a first-order kinetic plot of the experimental data at 430 nm, $[H_2O_2] = 10^{-1}$ M, [lum] = 10^{-4} M, dose = 8.0 krad.

Table III. Rate Constants for the Decomposition of the Peroxide Adduct

pH	$k \times 10^{-3}$, s^{-1}	dose, krad	$c_{H_2O_2}$, M	c_{lum}, M	method
7.7	1.71	3.7	0.5	10^{-3}	Adk at 450 nm
7.7	2.06	8.1	0.5	10^{-3}	Adk at 450 nm
7.7	2.06	8.0	0.5	10^{-3}	Adk at 450 nm
7.7	2.30	7.5	0.5	10^{-3}	Abk[a] at 385 nm
7.7	2.04	4.6	0.5	10^{-3}	Abk[a] at 385 nm
9.3	2.95	8.2	0.1	10^{-4}	Adk at 450 nm
9.3	3.12	15.1	0.1	10^{-4}	Adk at 450 nm
9.3	2.44	8.2	0.06	10^{-4}	Adk at 400 nm
9.3	2.82	8.0	0.06	10^{-4}	Adk at 400 nm
9.3	3.20	7.4	0.06	10^{-4}	Adk at 425 nm
9.3	3.67	7.3	0.06	10^{-4}	Adk at 450 nm
9.3	2.67	5.6	0.1	10^{-3}	Chdk
9.3	3.5	8.8	0.06	1.2×10^{-4}	Chdk
9.3	3.3	17.9	0.2	2×10^{-4}	Chdk
11.0	180	3.6	0.1	10^{-3}	Chbk
11.0	170	4.3	0.1	10^{-3}	Chbk
11.0	190	5.5	0.1	10^{-3}	Chbk
11.0	200	15.0	0.1	10^{-3}	Chbk
11.0	180	13.0	0.1	10^{-3}	Chbk

[a] Absorbance buildup kinetics. See Table II for the denotion of other methods.

recorded in order to ensure that the major part of lum· is consumed according to reaction 3. Figure 3 shows such a spectrum at pH 9.3. As can be seen from the figure, the spectrum of the recombination product (curve b) shows a weak absorbance above 400 nm. A final spectrum stable over at least several milliseconds (curve c) is obtained. In Table II, the kinetic measurements along with the determined k_c values are summarized. Inserted in Figure 3 is a first-order kinetic plot of the transient absorption. It consists of two straight lines with different slopes. The initial slope yields k_c, whereas the second yields the rate constant of the decay of curve b. As seen in Table III this rate is identical with that found from chemiluminescent measurements. Based on this identity we assign the transient spectrum of curve b to the peroxide adduct. Again, a systematic decrease of k_c from 1.4×10^9 to about 2×10^8 M^{-1} s^{-1} between pH 7.7 and 11 is observed, a fact that further confirms the pK_a step of the luminol radical.

Effect of pH on the Integrated Chemiluminescence Intensity. Figure 4 shows the integrated light intensity as a function of pH at two different ratios between H_2O_2 and luminol. The two curves display a monotonous increase with increasing pH up to about pH 11, but they differ both in absolute light yield and apparent pK_a value. This result shows the competition between H_2O_2 and luminol for OH· radicals where the increase with pH reflects the

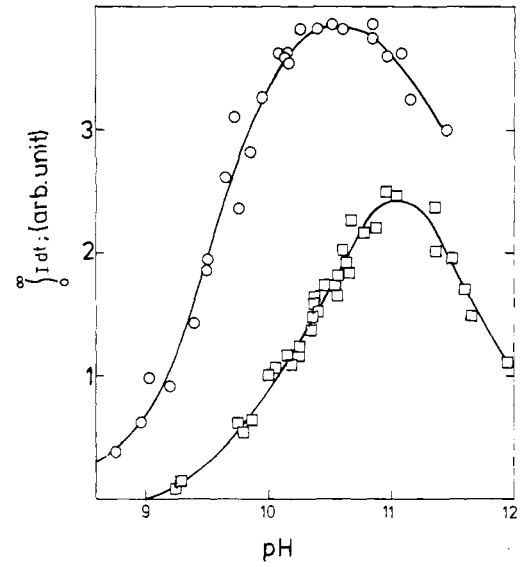

Figure 4. Integrated light intensity as a function of the pH. lum 10^{-3} M (○), 10^{-2} M H_2O_2 (□), 10^{-3} M H_2O_2.

dissociation step of H_2O_2 into its anion. The decrease at high pH matches rather well the decrease of the fluorescent quantum yield of the phthalate ion. The shift in the apparent pK_a values is smaller than would be predicted on the assumption that H_2O_2 dissociation is the only pH effect. To investigate the remaining, if any, pH effect, H_2O_2 titrations similar to those in Figure 1 were performed at three different pH values. As shown previously the maximum obtained in this type of experiments corresponds roughly to $[O_2^-\cdot]_0/[\text{lum}\cdot]_0 = \text{constant} \simeq 1$. Thus, the maximum light integrals can be compared without the interference of the H_2O_2 equilibrium. To state it differently: at a given dose the same total amount of the peroxide adduct is produced irrespective of the pH. The maxima increase with increasing pH, which proves that there is another pH effect outside the above-mentioned trivial one. The pK_a value 9.3 ± 0.3 was found.

Generally speaking, the total chemiluminescence quantum yield ϕ_{cl} can be represented as a product of three factors:

$$\phi_{cl} = \phi_c \phi_E \phi_{fl} \quad (4)$$

ϕ_c is the chemical quantum yield; ϕ_E is the fraction of excited molecules on the "correct" pathway; ϕ_{fl} is the fluorescence quantum yield of the end product. ϕ_{fl} has been determined by Seliger.[17,18] His results show that between pH 7 and 11 ϕ_{fl} is essentially constant and roughly equal to 0.30. After pH 11, ϕ_{fl} decreases strongly.

Assuming that ϕ_E is independent of pH, the light integral between pH 7 and 11 should be a good measure of the chemical yield ϕ_c. Therefore the results of the "maximum-value" titrations are indicative of an alternative chemical path, which does not lead to light production and whose importance increases with decreasing pH.

The Dark Reaction. Consider Figure 5 together with the insets. First, the insets show that the absorbance of the transient at 385 nm does not approach the base line monotonously, which it should if the final product is 3-aminophthalate. Instead, its initial decrease is followed by a subsequent increase toward a final absorbance. The two spectra which are taken when the peroxide intermediate is known to have formed, and later, when the absorbance has obtained a final value, differ markedly from each other, displaying an isobestic point. The final product formed in the "dark" reaction is yellow and has a stronger absorption at 390 nm than the peroxide adduct.

Table III shows the results of the kinetic measurements. A first-order rate constant at pH 7.7 is obtained with the value (2

(17) H. H. Seliger in "Light and Life", W. D. McElroy and B. Glass, Eds., The John Hopkins Press, Baltimore, 1961, p 200.
(18) J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **15**, 227 (1972).

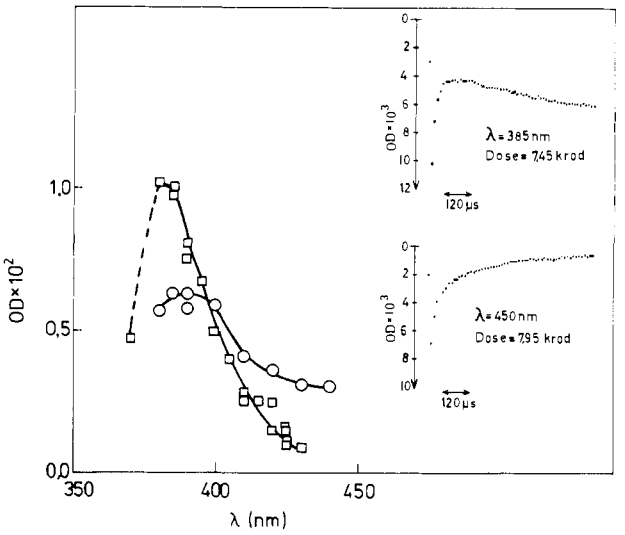

Figure 5. Transient absorption spectra of an aqueous solution containing 10^{-1} M H_2O_2 and 9×10^{-5} M luminol at pH 7.7. The peroxide adduct spectrum (○) is recorded 140 μs after the end of the electron pulse while the "dark" product spectrum (□) is recorder 1.5 ms after the end of pulse. The insets display the time behavior of transient absorptions at fixed wavelengths.

± 0.5) × 10^3 s^{-1}. Since the signals are rather small the closeness of the values could be spurious. For this reason the error margin is estimated.

The Direct Light-Producing Step. Before enumerating the results a short digression will be made to describe the nature of a typical chemiluminescence curve (i.e., intensity vs. time). Consider the following scheme:

$$\text{lum}\cdot + O_2^{-}\cdot \xrightarrow{k_c} (\text{lum}O_2)^{-} \xrightarrow{k} \text{end product} + h\nu \qquad (5)$$

k is the rate constant for decomposition of the peroxide adduct to yield light. The following relationship is obtained for the light intensity I.

$$I = d h\nu/dt = \gamma k[(\text{lum}O_2)^{-}] \qquad (6)$$

$$d[(\text{lum}O_2^{-})]/dt = k_c[\text{lum}\cdot][O_2^{-}\cdot] - k[(\text{lum}O_2)^{-}] \qquad (7)$$

γ is a composite apparatus constant. Expressing $[(\text{lum}O_2)^{-}]$ by I and rearranging we obtain

$$dI/dt + kI = \gamma k k_c[O_2^{-}\cdot][\text{lum}\cdot] \qquad (8)$$

Equation 8 cannot be solved analytically unless simplifying assumptions are introduced. By putting $[O_2^{-}\cdot]_0 \gg [\text{lum}\cdot]_0$ we obtain the equation for the familiar first-order consecutive sequence. This has the standard solution:

$$I = \frac{k_c[O_2^{-}\cdot]_0[\text{lum}\cdot]_0}{k - k_c[O_2^{-}\cdot]_0}(e^{-k_c[O_2^{-}\cdot]_0 t} - e^{-kt}) \qquad (9)$$

In the general case, the rate constant will have to be simulated from the chemiluminescence curve. However, in the limiting cases where $k \gg k_c[O_2^{-}\cdot]_0$ or vice versa, both constants can be measured directly. At short times, one of the exponentials is effectively constant. Therefore a ln $(I_{max} - I)$ vs. t plot will have the slope equal to the larger rate constant. At long times, a ln I vs. t plot on the decay part of the curve will yield the smaller rate constant.

Figure 6 shows typical chemiluminescence curves at pH 9.3 and 11. All curves are measured under pseudo-first-order conditions. The curves display similar decay characteristics, whereas the rise part is much more rapid at pH 11. Tables II and III present the k and k_c values which are obtained from the curves. As can be seen k has the value 1.8×10^5 s^{-1} at pH 11 and drops to about 3000 s^{-1} at pH 9.3. These results can be rationalized in the following way. It is assumed that there is an acid–base equilibrium of the peroxide adduct which is marked pK_a in the reaction scheme.

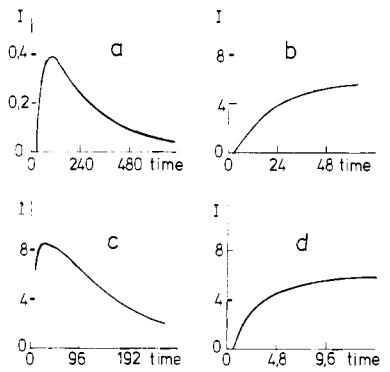

Figure 6. Chemiluminescent intensity as a function of time, where (a) and (c) depict the overall time behavior while (b) and (d) represent the buildup portion of the chemiluminescence. Time scale in μs. (a) pH 9.3, 10^{-4} M luminol, 10^{-1} M H_2O_2, 9.5 krad; (b) pH 9.3, 10^{-4} M luminol, 10^{-1} M H_2O_2, 8.4 krad; (c) pH 11.0, 10^{-3} M luminol, 10^{-1} M H_2O_2, 8.6 krad; (d) pH 11.0, 10^{-3} M luminol, 10^{-1} M H_2O_2, 8.2 krad.

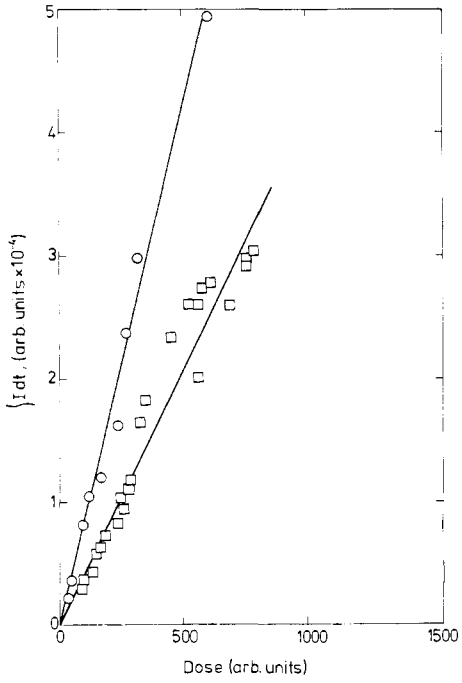

Figure 7. Integrated light intensity as a function of dose: (○) pH 11.0, 10^{-3} M luminol, 7×10^{-3} M H_2O_2; (□) 10^{-3} M luminol, pH 10.0, saturated with a 90% N_2O + 10% O_2 mixture. The dose scale is linear with the value 1000 corresponding to 13 krad.

The protonated form undergoes a dark reaction with a rate constant of (2 ± 0.5) × 10^3 s^{-1}. The basic peroxide adduct is involved in a rapid intramolecular reaction which ultimately forms the excited state and yields chemiluminescence. The rate constant k_p for this process should be larger than or equal to 2×10^5 s^{-1}. The accuracy of our results permits only the calculation of the range for the pK_a value of the peroxide. In the calculations the limits $1500 \le k_d \le 2500$ s^{-1} and $1.8 \times 10^5 \le k_p \le 10^6$ are used where the upper limit 10^6 appears a reasonable assumption. Setting $k = k_d$ at pH 9.3 (obtained from the "maximum-value" titrations), the limits of the pK_a value of the peroxide adduct were calculated: $11.1 < pK_a < 12.1$, where the upper limit is dependent on the highest value assumed for k_p. This is a fairly reasonable value for a peroxide (cf. pK_a for H_2O_2 = 11.7). With the evidence at hand a nitrogen-centered peroxide adduct cannot be ruled out.

Determination of the Relative Quantum Yield. Würzberg et al.[19] have rerun the experiments of Baxendale[5] and measured the quantum yield in the luminol–O_2 system. By using that system as reference, we are able to estimate the chemiluminescence

(19) E. Würzberg and Y. Haas, *Chem. Phys. Lett.*, **55**, 250 (1978).

quantum yield in our system. Figure 7 presents the results of this determination. We obtain for ϕ_{cl} the approximate value 0.10. Though this value contains the cumulative errors of two relative measurements, its mere largeness indicates that the chemical step studied here is really the one directly responsible for light generation. It should be pointed out that here ϕ_{cl} is defined as the ratio of the number of photons produced to the number of luminol molecules consumed.

Some Reflections on the Luminol–O_2 System. Upon comparison of the luminol–O_2 system studied by Baxendale[5] and Würzberg et al.[14] with the present system, the following striking similarities are observed.

(a) The integrated light intensity vs. pH displays approximately the same apparent pK_a value.

(b) The light obtained remains constant in both systems between pH 10 and 11.

(c) The rise time for chemiluminescence decreases monotonously with increasing pH.

These observations strongly suggest that in both cases the same crucial intermediate (namely, the peroxide adduct) is operative. In the O_2 system, the formation of the peroxide adduct should be the result of a dismutation of the peroxy radicals. If so, formation of the peroxide could be paralleled by the production of azaquinone and O_2. Indeed, Baxendale and Würzberg et al. observe an increase in absorbance between 500 and 600 nm, a spectral region where azaquinone has a sizable extinction coefficient.[16] The lower quantum yield found in the luminol–O_2 system is most probably due to competing reactions in the dismutation step of the peroxy radicals.

Relating the Present Work to Existing Theories. Finally, relating the present reaction scheme with modern theories on chemiluminescence as proposed by White et al.,[20] McCapra et al.,[21] and Schuster et al.[22] is appropriate. First it will be noticed that the kinetic findings in this work in no way contradict or confirm the presence of an electron transfer in the final excitation step. At present we are not able to assess the nature of the decomposition step. Reaction schemes[20,21] where expulsion of nitrogen is followed by further steps are not inconsistent with our results. Since only one kinetic step can be measured in the decay of the peroxide, it transpires that, if further steps exist, they should be very rapid indeed ($k > 10^6$ s^{-1}). Further work will be done to determine the activation parameters of this reaction.

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(22) (a) J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977); (b) *ibid.*, **100**, 4496 (1978).

Mechanistic Change in Acid-Catalyzed Hydrolysis of Silyl Vinyl Ethers[1]

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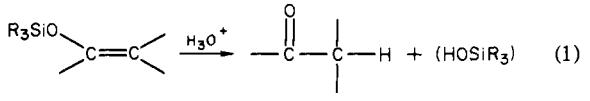
Abstract: *tert*-Butyldimethylsilyl vinyl ethers *t*-BuMe$_2$SiOCR=CH$_2$ hydrolyze in 50% CH$_3$CN–H$_2$O with general and specific acid catalysis and a linear dependence of log k_{H^+} on σ_p^+(R), indicating that the reaction occurs with rate-determining proton transfer to carbon (the Ad_E2 mechanism). By contrast the rates of trimethylsilyl vinyl ethers Me$_3$SiOCR=CH$_2$ are not correlated by σ_p^+(R) but still depend on proton and general acid concentrations. Nucleophilic attack on silicon is implicated in the rate-determining step of the latter compounds, and the possibilities for the details of this process are considered.

Trialkylsilyl vinyl ethers have become of pervasive importance in synthetic organic chemistry,[2] but studies of their reaction mechanisms have been conspicuously neglected. Hydrolysis of the silyl vinyl ethers to carbonyl compounds (eq 1) is an important transformation of these materials, and we have now studied the kinetics of the acid catalysis of the process.



(1)

Results

Silyl vinyl ethers of representative structural types were prepared by known procedures[3,4] for rate studies. The solubilities of these substrates in water were low so 50% by volume H$_2$O–acetonitrile solutions were utilized for the kinetic measurements. Rates were measured by monitoring the change of the alkene or carbonyl chromophore by UV spectroscopy.

For the least reactive compound studied, *t*-BuMe$_2$SiOCH=CH$_2$, the rate could be conveniently monitored by using HCl catalyst, and a linear dependence of rate on HCl concentration in the range 0.03–0.12 M was observed. For all other substrates acetate or formate buffers were used as catalysts. The rate law $k_{obsd} = k_{H^+}[H^+] + k_{HA}[HA]$ where HA is the buffer acid was

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