# Oxidation of Luminol by Chlorine Dioxide

Formation of 5-Aminophthalazine-1,4-dione

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The pH-dependent reaction rate between luminol and chlorine dioxide has been determined. The net oxidation reaction proceeds in two steps. The first of these is the formation of a luminol– $ClO_2$  adduct. This adduct, which is unreactive towards oxygen, reacts rapidly with itself or with a second  $ClO_2$  molecule. The final product has a broad absorbance between 450 and 650 nm. An identical absorbance is produced when luminol is oxidized by HOCl. The species displaying this absorbance is very reactive towards  $OH^-$  and undissociated luminol. In the presence of hydrogen peroxide and at pH > 7 the absorbance disappears. At the same time an intense chemiluminescence is observed, the decay of which is quantitatively in agreement with the decay of the 450-650 nm absorbance. From these findings it is concluded that the oxidation product of luminol with  $ClO_2$  is 5-aminophthalazine-1,4-dione.

The two-electron oxidation product of luminol, 5-aminophthalazine-1,4-dione (azaquinone), looms large in the chemiluminescent literature as a (1) sometime and (2) ubiquitous intermediate in the chemiluminescent process of luminol. While the second claim is neither proved, nor is it very probable, there is some fairly compelling evidence for the validity of the first one.

An important breakthrough from hypothesis to experiment is marked by the actual isolation of some relatively stable azaquinones.<sup>1, 2</sup> In this way it could be demonstrated that the azaquinones yield chemiluminescence in the presence of aqueous alkaline  $H_2O_2$ . Furthermore, the chemiluminescence spectra are similar to those obtained upon catalytic oxidation of the corresponding hydrazides.

While these findings prove beyond doubt that azaquinones are reasonable intermediates, they fall short of demonstrating the participation of the latter in the actual chemiluminescent process of the hydrazides.

Omote *et al.*<sup>3</sup> have been able to obtain small amounts of a Diels-Alder adduct of 5-aminoazaquinone in a  $Fe(CH)_6^{3-}$  catalysed chemiluminescent system based on luminol. However, two objections can be raised to their claim of having proved the azaquinone to be an intermediate in this system. (1) The amount of the isolated adduct is far from quantitative. (2) It is conceivable that cyclopentadiene is reactive even towards a luminol radical with 'azaquinoid' properties.

Kinetic evidence for the participation of the azaquinone in the chemiluminescence of luminol comes mainly from the work of Rauhut *et al.*<sup>4</sup> However, due to the slow oxidation of luminol by persulphate, the azaquinone could never be detected in their system. Finally, the azaquinone has been observed as a transient<sup>5</sup> by stopped-flow upon oxidation of 2,3-naphtalic hydrazide with hypochlorite.

The present work has two objectives. First, it will demonstrate the mechanism of azaquinone formation in the aqueous luminol– $ClO_2$  system. Subsequently, the chemical properties of the *in situ* generated azaquinone will be investigated.

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Note that chlorine dioxide, which here is generated by pulse radiolysis,<sup>6</sup> is not a 'phantom' but a stable radical. The only reason why it is generated pulse radiolytically is the expedient of fast kinetic measurements on the time evolution of the system. Therefore, the present experiments are equivalent to 'stopped-flow' experiments with microsecond time resolution where the 'mixing time' corresponds to the time during which chlorine dioxide is generated.

# EXPERIMENTAL

The equipment, analytical methods and materials are described in ref. (6). Luminol (P.A. > 97% Egachemie) was found by thin-layer chromatography to contain minor amounts of two impurities which could be removed by recrystallization of the luminol monosodium salt in water. Comparison of the radiolytic yields and kinetics obtained in pulse-radiolysis experiments on purified and commercial luminol showed no significant difference. Hence luminol was used as received.

#### RESULTS

# THE SEARCH FOR A SUITABLE OXIDANT

The OH radical, which is produced in the radiolysis of water, oxidizes luminol rapidly to the luminal radical. To obtain the azaquinone a second one-electron oxidation step is necessary. All our efforts to achieve this second step by addition of  $Fe(CN)_6^{3-}$  or by generation of initial OH<sup>-</sup> concentrations in more than twofold excess over luminol proved unsuccessful. Recently, it has been observed that  $ClO_2^{\circ}$  yields an intense and rapid chemiluminescence<sup>7</sup> with luminol and  $H_2O_2$ . This observation now forms the basis of the quantitative determination of small amounts of  $ClO_2^{\circ.8}$  Thus it appeared worthwhile to scrutinize the oxidation mechanism of  $ClO_2$  in the luminol system.



FIG. 1.—Bimolecular experimental rate constant for the disappearance of ClO<sub>2</sub><sup>-</sup> due to its reaction with luminol, plotted as a function of pH: ○, ClO<sub>2</sub> disappearance measured at 360 nm; △, azaquinone build-up measured at 550 nm. The inserts show the dependence of the measured rate constants on luminol concentrations: ▲, pH 11.1; ○, pH 9.6; △, pH 8.5.

# THE REACTION BETWEEN $ClO_2$ and luminol

At luminol concentrations of *ca*.  $10^{-4}$  mol dm<sup>-3</sup> it is possible to observe the decay of the ClO<sub>2</sub> absorbance at 360 nm. Fig. 1 displays the bimolecular rate constant between luminol and ClO<sub>2</sub> as a function of pH as calculated from the measured decay rates at 360 nm. The rate constant increases monotonically with increasing pH. Furthermore, the inserts prove that the reaction is strictly overall second order. At pH values below 7.5 the rate decreases towards zero or very low values. This fact can only be interpreted as meaning that undissociated luminol (LH<sub>2</sub>) is relatively inert towards ClO<sub>2</sub>. At pH 14 (not shown in the figure) the rate constant  $1.6 \times 10^8$  s<sup>-1</sup> mol<sup>-1</sup> dm<sup>3</sup> was found. This behaviour can be attributed to the very high reactivity of doubly dissociated luminol (L<sup>2-</sup>) towards ClO<sub>2</sub>. The intermediate part (7.5 < pH < 11) which coincides with the monodissociated form of luminol (LH<sup>-</sup>) will be discussed later. The overall shape of the curve gives ample evidence of the electrophilic character of the ClO<sub>2</sub> attack. Expressed in simple terms, ClO<sub>2</sub> is attracted by 'bare' electrons.

INTERMEDIATES INVOLVED IN THE OXIDATION OF LUMINOL BY  $ClO_2^{\cdot}$ 

Upon reaction of  $ClO_2^{\circ}$  with luminol, the disappearance of  $ClO_2^{\circ}$  is concomitant with the following events:

(a) At luminol concentrations below  $2 \times 10^{-3}$  mol dm<sup>-3</sup> or at high doses (the initial concentration of ClO<sub>2</sub> being > ca.  $4 \times 10^{-5}$  mol dm<sup>-3</sup>) combined with luminol concentrations ranging from  $2 \times 10^{-3}$  to  $1 \times 10^{-2}$  mol dm<sup>-3</sup>, a broad absorbance centred around 550 nm appears directly. In the pH interval studied, the rate constant for the appearance of this absorption is identical to that shown in fig. 1.

(b) At luminol concentrations ranging from  $2 \times 10^{-3}$  to  $1 \times 10^{-2}$  mol dm<sup>-3</sup> and initial ClO<sub>2</sub> concentrations below  $4 \times 10^{-5}$  mol dm<sup>-3</sup> (corresponding to doses < 5 krad) a transient absorbance appears below 470 nm. During this time, the build-up of the







FIG. 3.—Transient spectra obtained from a  $10^{-2}$  mol dm<sup>-3</sup> luminol, 1 mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> solution at pH 9.2 and *ca.* 1.9 krad dose: (- - -) initial ClO<sub>2</sub> absorbance as calculated from ref. (6);  $\bigcirc$ , 36  $\mu$ s after the electron pulse;  $\triangle$ , 475  $\mu$ s after the electron pulse. The inserts show from top to bottom: The calculated (from fig. 1) disappearance of ClO<sub>2</sub>. The build-up of the absorbance at 550 nm. The build-up and decay of the absorbance at 430 nm.

550 nm absorbance is also observed. The latter has a time lag of ca. 10  $\mu$ s. During the decay of the < 470 nm absorbance the 550 nm absorption increases further to a 'semi-stationary' level. This level is proportional to the initial ClO<sub>2</sub> concentration and hence the dose (*viz.* fig. 2).

For case (b) the transient spectra and their dynamics are presented in fig. 3. At this point some additional experiments concerning the species absorbing below 470 nm, henceforth denoted by A, will be described.

In solutions with pH in the range 8.5-11.0 containing  $10^{-1}$  mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> and luminol (between  $3 \times 10^{-3}$  and  $10^{-2}$  mol dm<sup>-3</sup>), the yield of A is not linearly proportional to the dose. However, from the initial slope of the yield against dose curve at doses between 0.3 and 2.5 krad the Ge(430 nm) value for A was determined to  $1.2 \times 10^4$ . This value combined with the initial part of the build-up of A enables us to calculate the rate constant for the reaction

by eqn (1) 
$$\ln [G\varepsilon(430 \text{ nm}) \times \text{dose} - \text{O.D.}] = k[\text{luminol}]t.$$
(1)

For this reaction the initial slope obtained from an O.D. against time plot should be given by  $\tan \alpha = k\epsilon(430 \text{ nm})$  [CIO.] [luminol]

$$= k\varepsilon(430 \text{ nm}) [\text{luminol}]G(\text{ClO}_2) \times \text{dose}.$$

In 1 mol dm<sup>-3</sup> ClO<sub>2</sub> solutions containing 10<sup>-2</sup> mol dm<sup>-3</sup> luminol the proportionality

between tan  $\alpha$  and dose was confirmed, and by assuming that all ClO<sub>2</sub> reacts with luminol to form A [*i.e.*  $G(A) = G(ClO_2)$ ]k was calculated. These two equivalent experimental procedures yielded the k-value  $(3.0 \pm 0.5) \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$ , which is constant throughout the pH interval studied.

The extinction coefficient of A at 430 nm [ $\epsilon$ (430 nm) = 2200 ± 400] was determined by two independent methods, with similar results.

(1) The first method makes use of the extinction coefficient of the 550 nm species (vide infra), henceforth denoted by Az and the stoichiometry

$$2A \xrightarrow{2k} Az$$

This stoichiometry is confirmed by the second-order decay of A

$$2k/\epsilon(430 \text{ nm}) = 4.1 \times 10^5 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$$

and the proportionality between the yield of Az and the initial  $ClO_2$  concentration (see fig. 3).

(2) In a solution containing  $10^{-1}$  mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> and  $10^{-2}$  luminol  $G(ClO_2)$  is assumed to be 4.5 on the following grounds: at the end of the electron pulse an absorbance identical to that of the luminol radical<sup>9, 10</sup> appears in the above solution. With increasing ClO<sub>2</sub><sup>-</sup> concentration this initial absorbance diminishes and is absent once ClO<sub>2</sub><sup>-</sup> is in a 100-fold excess over luminol. Also, this initial absorbance is roughly proportional to the reciprocal of the ClO<sub>2</sub><sup>-</sup> concentration. This behaviour is interpreted in terms of the unspecified precursor to ClO<sub>2</sub><sup>-,6</sup> which directly oxidizes luminol to the luminol radical.

From the known extinction coefficient of the luminol radical<sup>10</sup> its yield in the above solution is determined to be G = 2.3. Assuming that the species which in this case produces the luminol radical would generate the equivalent amount of ClO<sub>2</sub> in the absence of luminol, the actual yield of ClO<sub>2</sub> is estimated to be  $G(ClO_2) = 6.8 - 2.3 = 4.5$  where G = 6.8 is the yield of ClO<sub>2</sub> in a 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> solution.<sup>6</sup>

# CHEMISTRY OF THE SPECIES RESPONSIBLE FOR THE BROAD ABSORBANCE AROUND 550 nm

Before any meaningful investigation of this species can be undertaken one must establish the exact stoichiometry of its formation from luminol and  $ClO_2^{\cdot}$ . In addition it is necessary to investigate whether hypochlorite (the formation of which is always concomitant with that of  $ClO_2^{\cdot}$  in pulse radiolysis<sup>6, 11</sup>) yields the same product as  $ClO_2^{\cdot}$ , and if so with what stoichiometry. By mixing varying amounts of  $ClO_2$  or HOCl with luminol in a 'stopped-flow' apparatus it was found that the products formed displayed internally identical absorbance spectra which were also identical to the transient spectrum found pulse radiolytically (see fig. 3). Thus both  $ClO_2$  and HOCl form the same product, henceforth denoted by Az. Table 1 shows the results from the 'stopped-flow' experiment. The extinction coefficient of Az at 550 nm was calculated from the experimental absorbance with the assumptions:

$$luminol + 2ClO_2 \rightarrow Az$$
$$luminol + HOCl \rightarrow Az.$$

Of course, when ClO<sub>2</sub> was in large excess, it was assumed that all luminol yielded Az. The excellent internal consistency of the calculated value of  $\varepsilon(550 \text{ nm})$  proves unambiguously that the assumed stoichiometries are correct. Note particularly that addition of 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> to the ClO<sub>2</sub> solution does not affect the yield of Az.

#### OXIDATION OF LUMINOL BY $ClO_2$

pН	C <sup>a</sup> (luminol)/ 10 <sup>-4</sup> mol dm <sup>-3</sup>	$C^{a}(\text{ClO}_{2})/10^{-4} \text{ mol dm}^{-3}$	$C^{a}(\text{HOCl})/10^{-4} \text{ mol dm}^{-3}$	[0.d.(550)] <sub>meas</sub>	$[\epsilon(550)]_{calc}$
8.76	2	0.80		0.22	2750
8.21	12.5	2.5		0.62	2480
8.21	12.5	2.5		0.61	2440
8.21	1.3	5.0	_	0.73	2800
8.0	5.0	2.5	_	0.68	2720
7.05	1.0	5.0	_	0.51	2550
7.05	1.0	5.0		0.51	2550
8.03	1.0	12.5		0.55	2750
7.01	2.0	_	0.80	0.45	2810
8.76	2.0	—	0.26	0.16	3080
8.76	1.0	—	1.8	0.52	2600
					$\bar{\varepsilon} = 2700 \pm 200$

TABLE 1.—STOPPED-FLOW DETERMINATION OF  $\varepsilon(Az)$  at 550 nm

<sup>a</sup> Initial concentrations in reaction chamber; <sup>b</sup> 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub><sup>-</sup> was added.

Recent reports<sup>12, 13</sup> claiming that the hydrazide, HOCl stoichiometry is different from 1:1 are at variance with our observations, although the product spectrum reported<sup>13</sup> is similar to that of Az. Before embarking on a quantitative comparison between the yields of Az obtained by stopped-flow and pulse radiolysis, respectively, it will be helpful to consider the various reactions of Az. Fig. 4 presents the experimentally obtained first-order rate constants for the disappearance of Az as a function of pH. The different curves correspond to different combinations of the concentrations of luminol and  $ClO_2^-$ , respectively. All experiments were performed at high initial  $ClO_2$ concentrations, thus complying to case (a) (vide supra). Where possible, the pulse radiolytic measurements were complemented by some 'stopped-flow' values. Once more, the excellent agreement between these measurements confirms the identity of the 'two' Az products regardless of the method of their generation. It is also seen that 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub> does not modify the reactivity of Az. Apart from individual variations between the curves, two gross features can be generally discerned. (1) Az is subject to OH<sup>-</sup>-catalysed hydrolysis at high pH. (2) At low pH Az reacts with undissociated luminol  $(LH_2)$  with the concomitant appearance of a new and stable absorption at ca. 470 nm. As to the behaviour of the individual curves, note that the lower the luminol concentration, the lower the pH where a curve deflects from the straight line with slope 1.

At high doses, the formation and decay of Az constitute a first-order consecutive reaction sequence. When the build-up and decay rate of Az assume comparable magnitudes the measured decay rate will be slower than the true one. The true build-up and decay rates approach each other with decreasing luminol concentration and increasing pH. Therefore, it is reasonable to assume that the true decay rate constants follow the straight line with slope 1 in fig. 4. The deviation of the 1 mol dm<sup>-3</sup> ClO<sub>2</sub> solution from the rest should be at least partly ascribed to the ionic strength effect. With the above proviso the following rate constants are obtained

$$k_1(Az+OH^-) = (4 \pm 1) \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$$
  
 $k_2(Az+LH_2) = (1.3 \pm 0.2) \times 10^4 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3.$ 



FIG. 4.—Measured first-order decay rate of the azaquinone as a function of pH:  $\blacksquare$ , measured with 'stopped-flow' (luminol concentration  $\approx 10^{-4} \text{ mol dm}^{-3}$ );  $\bigcirc$ ,  $10^{-4} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;  $\bigcirc$ ,  $10^{-3} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;  $\bigcirc$ ,  $10^{-2} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;  $\triangle$ ,  $10^{-2} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;  $\triangle$ ,  $10^{-2} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;  $\triangle$ ,  $10^{-2} \text{ mol dm}^{-3}$  luminol,  $10^{-1} \text{ mol dm}^{-3}$  ClO<sub>2</sub><sup>-</sup>;



FIG. 5.—Pulse-radiolytic yield of azaquinone as a function of pH: (a)  $10^{-3} \mod dm^{-3} \ luminol$ ,  $10^{-1} \mod dm^{-3} \ ClO_2^-$ ;  $\triangle$ , experimental values:  $\blacktriangle$ , corrected values; (b)  $10^{-2} \mod dm^{-3} \ luminol$ ,  $10^{-1} \mod dm^{-3} \ ClO_2^-$ ; (c)  $10^{-2} \mod dm^{-3} \ luminol$ ,  $1 \mod dm^{-3} \ ClO_2^-$ .

# 02 OXIDATION OF LUMINOL BY $ClO_2$

Fig. 5 presents the maximum yield of Az as a function of pH for the three different solutions differing in their composition with respect to  $[ClO_2^-]$  and [luminol]. The *G* values are calculated from the measured absorbance at 550 nm by use of the value  $\varepsilon(550 \text{ nm}) = 2700 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ . All three curves in fig. 5 display a transition within *ca*. 2 pH units from a high-yield to a low-yield level with an apparent p $K_a$  value. Since the sum of  $G(ClO_2)$  and  $G(OCl^-)$  is not dependent on pH<sup>6</sup> this behaviour can only be accounted for by kinetic effects. The key to the pH behaviour of the curves lies in the reactivity of hypochlorite towards luminol. It has been shown<sup>7, 12</sup> that while HOCl is reactive towards luminol  $[k(HOCl + luminol) \approx 5 \times 10^5 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3] \text{ OCl}^-$  manifests no measurable rate.<sup>12</sup> This fact coupled with the p $K_a$  value. At high pH values a downward curvature away from the plateau is observed on all curves, this effect being more pronounced in  $10^{-3} \text{ mol} \text{ dm}^{-3}$  luminol solution.

Consider the measured first-order reaction sequence at initial  $ClO_2$  concentration > 4 × 10<sup>-5</sup> mol dm<sup>-3</sup>

luminol (in excess) + 
$$\operatorname{ClO}_2 \xrightarrow[\operatorname{ClO}_2]{k_o \text{ (pH)}} \operatorname{Az} \xrightarrow[\operatorname{OH}^-]{k_1}$$
 products.

It can be shown that the following relationship holds.

$$[Az]_0 = [Az]_{meas} \times K^{(K/K-1)}$$

Here  $[Az]_0$  is the final concentration of Az if the latter were a stable product with no subsequent decay.  $[Az]_{meas}$  is the maximum measured yield of Az and

$$K = \frac{k_1 [\text{OH}^-]}{k_0 [\text{luminol}]_{\text{tot}}}$$

where  $k_0$  and  $k_1$  are defined above. The pH-dependent rate constant  $k_0$  is taken from fig. 1 while for  $k_1$  the value  $4 \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3$  is used. This correction, which is shown for the  $10^{-3}$  mol dm<sup>-3</sup> luminol curve, demonstrates that in the ClO<sub>2</sub> oxidation of luminol the integral yield of azaquinone is pH-independent.

By use of  $\varepsilon(Az)$  at 550 nm obtained from the 'stopped-flow' measurement and the yield of ClO<sub>2</sub> in 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub> solutions [ $G(ClO_2) = 6.8$ ]<sup>6</sup> the yield of Az in the pulse radiolytic system (10<sup>-3</sup> mol dm<sup>-3</sup> luminol and 10<sup>-1</sup> mol dm<sup>-3</sup> ClO<sub>2</sub>) is determined to *ca*. 100 ± 5% by the formula:

yield (Az) = 
$$\frac{G(Az)}{\frac{1}{2}G(ClO_2)} \times 100\%$$
.

In 10<sup>-3</sup> mol dm<sup>-3</sup> luminol 0.1 mol dm<sup>-3</sup> ClO<sub>2</sub> solutions at pH 7, where on the timescale of the measurements HOCl, too, participates in the production of Az, a yield of Az = 100±10% was found. This yield is based on  $G(\text{ClO}_{tot}) = 3.0\pm0.3$ ,  $G(\text{ClO}_2) = 6.8\pm0.2^6$  and a kinetic correction (10% increase) as described for ClO<sub>2</sub> but with the pertinent pseudo-first-order rate constants [ $k(\text{HOCl}+\text{LH}^-) = 5 \times 10^2 \text{ s}^{-1}$ ,  $k(\text{Az}+\text{LH}_2) = 13 \text{ s}^{-1}$ ].

When the luminol concentration is increased to  $10^{-2}$  mol dm<sup>-3</sup> in a  $10^{-1}$  mol dm<sup>-3</sup> ClO<sub>2</sub> solution [curve(b)] a lower yield of Az is obtained compared with that of curve (a). As pointed out before a precursor (X) to ClO<sub>2</sub> reacts directly with luminol at this concentration (instead of with ClO<sub>2</sub>) to form the luminol radical. The decrease in the yield of Az between curves (a) and (b) is matched by a corresponding initial production of the luminol radical. Upon increasing the ClO<sub>2</sub> concentration to 1 mol dm<sup>-3</sup> (10<sup>-2</sup> mol dm<sup>-3</sup> LH<sup>-</sup>) the yield of Az increases [curve (c)] and no initial formation of

the luminol radical is observed. Assuming a 100% yield of Az, the  $G(ClO_2)$  is calculated to be 8.9 from curve (c). This value is in fair agreement with the one presented in fig. 2 of ref. (6). Comparison of curve (a) with curve (b) reveals that G(HOCl) is not significantly effected by variation of the luminol concentration.

#### ANALYSIS OF GASEOUS END-PRODUCTS

Table 2 presents the yields of N<sub>2</sub> and O<sub>2</sub> under  $\gamma$ -radiolysis. In addition, the primary radiolysis of water produces H<sub>2</sub> with  $G \approx 0.4$ , this being close to the reported value.<sup>14</sup> The values from one-electron beam irradiation are also included in table 2 where the dose is established from the H<sub>2</sub> yield as determined by  $\gamma$ -radiolysis.

pН	C(luminol)/ mol dm <sup>-3</sup>	$C(ClO_2^-)/mol dm^{-3}$	dose/ krad	$G(N_2)$	<i>G</i> (O <sub>2</sub> )	dose rate/ krad h <sup>-1</sup>
7.2	10-3	10-1	33	0.9	< 0.1	396
10.2	10-3	10-1	33	7.0	< 0.1	396
11.5	10-3	10-1	33	7.1	< 0.1	396
11.2	10-2	10-1	20	3.1	0.45	396
11.2	$10^{-2}$	10-1	14	3.1	0.5	$2.5 \times 10^{9}$
11.0	10-2	10º	20	1.8	0.2	396

TABLE 2.— $\gamma$ -RADIOLYTIC G VALUES

Addition of known amounts of  $\text{ClO}_2$  and HOCl to  $10^{-3}$  mol dm<sup>-3</sup> luminol solutions at pH 10.5 showed that nitrogen is produced with a 1:2 and 1:1 stoichiometry, respectively. For HOCl this is in agreement with ref. (15). Up to 0.1 mol dm<sup>-3</sup>  $\text{ClO}_2^$ had no effect on the stoichiometry. Within the limits of experimental accuracy (10%) the following equality holds for the  $10^{-3}$  mol dm<sup>-3</sup> luminol+0.1 mol dm<sup>-3</sup>  $\text{ClO}_2^$ solution:

$$G(N_{2}) = G(HOCl) + G(ClO_{2})/2.$$

Thus the stoichiometry obtained from the 'stopped-flow' experiments is independently confirmed. At pH 7.2 the low yield of  $N_2$  in  $10^{-3}$  mol dm<sup>-3</sup> luminol solutions demonstrates the addition of Az to undissociated luminol as previously inferred from fig. 4.

The marked decrease of  $N_2$ -yields in  $10^{-2}$  mol dm<sup>-3</sup> luminol solutions indicates that the hydrolysis is not a simple one-step process.

#### EFFECT OF OXYGEN

The second-order decay of the 430 nm absorbance (species A) showed no significant change upon addition of  $6 \times 10^{-4}$  mol dm<sup>-3</sup> oxygen. This fact contrasts markedly with the high reactivity of O<sub>2</sub> towards the luminol radical.<sup>9, 16</sup> This inertness of species A towards O<sub>2</sub> is consistent with the observation that the yield of Az remains unchanged upon addition of O<sub>2</sub> (see fig. 2). 'Stopped-flow' measurements confirm the latter observation.

# DISCUSSION

# THE NATURE OF AZ

The question of prime importance is the identity of the species Az. The claim that Az is 5-aminophthalazine-1, 4-dione is based on the following observations. (1) In the oxidation of one molecule of luminol two molecules of  $ClO_2$ , but only one of HOCl

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are consumed to form one molecule of Az. (2) The oxidation of naphthalic hydrazide with HOCl yields the corresponding azaquinone, benzophthalazine-1,4-dione.<sup>5</sup> (3) The spectrum of Az at *ca*. 550 nm resembles that reported for naphtaphthalazine-1,4-dione, the chemiluminescence of the latter being similar to that of luminol.<sup>1</sup> (4) The rapid hydrolysis of Az yields N<sub>2</sub> quantitatively. (5) As shown in ref. (17) Az chemiluminesces intensely in the presence of HO<sub>2</sub><sup>-</sup> and yields 3-aminophthalate as an end-product. The reactivity of Az as demonstrated in fig. 4 gives a quantitative explanation as to why it has not yet been isolated.

The most reasonable end-product of the hydrolysis of Az is the anion of 3-amino-phthalaldehydic acid. Indeed the naphtha-aldehydic acid has been isolated as a product in the oxidation of naphthalic hydrazide by hypochlorite.<sup>5</sup> At pH  $\approx$  7 or at luminol concentrations  $\geq 10^{-2}$  mol dm<sup>-3</sup> the decrease in the yield of N<sub>2</sub> is explained by the reaction of Az with LH<sub>2</sub>.

#### THE REACTION MECHANISM

The experimental findings permit a fairly detailed establishment of the reaction mechanism summarized in scheme 1; some comments about certain points will follow.



SCHEME 1.-Reaction between ClO<sub>2</sub> and luminol.

The rate of the reaction between ClO<sub>2</sub> and luminol, measured as ClO<sub>2</sub> disappearance at luminol concentrations *ca.*  $10^{-4}$  mol dm<sup>-3</sup>, is pH-dependent in the pH range 8-11 where luminol in itself is a mono-anion. This fact contrasts with the pH-independent rate of the production of the adduct (A) as measured at 430 nm in  $2 \times 10^{-3}$  mol dm<sup>-3</sup> luminol solutions. At pH 11 the rate of adduct formation is about half of that of ClO<sub>2</sub> consumption. To explain these observations we invoke the acid–base equilibrium for the ClO<sub>2</sub> adduct of luminol with a  $pK_a \approx 9$ .

The dissociated form of the adduct  $(A^{2-})$  reacts rapidly with  $ClO_2$  whereas the undissociated form  $(AH^{-})$  must be relatively inert. The rate constant for the reaction of  $ClO_2^{+}$  with  $A^{2-}$  was estimated as

$$[K(A^{2-}+ClO_2) \simeq 3 \times 10^9 \text{ s}^{-1} \text{ mol}^{-1} \text{ dm}^3]$$

from measurements at such high initial  $ClO_2$  concentrations that the adduct showed no build-up and thus the steady-state approximation could be applied to its kinetics.

Note that the structure of the  $ClO_2$ -luminol adduct (AH<sup>-</sup>, A<sup>2-</sup>) is only tentative. The possibility of the addition of  $ClO_2$  to the oxygen atom of the enolic form of luminol cannot be ruled out on the basis of our experimental findings.

Any structural assignment of this adduct should be compatible with the following three properties: (1) the acid-base equilibrium of the adduct; (2) the close resemblance of the adduct spectrum to that of the luminol radical; (3) the low reactivity of the  $ClO_2$  adduct towards oxygen, whereas the opposite is true for the luminol radical. It is precisely the inertness towards oxygen which brings about the formation of Az, irrespective of the presence of oxygen.

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