Ozone Induced Chemiluminescence: Kinetics of Chemiluminescent Reaction between Ozone and Acridone in Acetic Acid*

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Ozone induced chemiluminescence (CL) of acridone in acetic acid is investigated. From preliminary spectral observations the CL emission is determined to be due to energy transfer from an excited species to acridone which emits at its fluorescence wavelength. UV-vis. spectra of the excited species as well as some of the products are obtained. From kinetic observations of the system, a reaction sequence according to which CL is produced upon reaction of an intermediary with ozone, is proposed. This intermediary is produced upon reaction of an initial oxidation product of acridone with another acridone unit and it is thought to be 10,10'biacridonyl. The rate constant of the first reaction step is determined to be $\approx 30\ \mathrm{M^{-1} \cdot sec^{-1}}$.

Die durch Ozon induzierte Chemilumineszenz von Akridon in Essigsäure wurde untersucht. Nach vorläufigen Spektraluntersuchungen ist die Emission die Folge einer Energieübertragung von einer angeregten Molekelart auf Akridon, das dann bei seiner Fluoreszenz-Wellenlänge emittiert. UV- und sichtbare Spektren der angeregten Molekelarten sowie einiger Produkte wurden aufgenommen. Auf Grund kinetischer Beobachtung wird eine Reaktionsfolge vorgeschlagen, in der Chemilumineszenz durch Reaktion eines Zwischenstoffes mit Ozon eintritt. Dieser Zwischenstoff entsteht durch Reaktion eines anfänglichen Oxydationsprodukts des Akridons mit einer weiteren Akridon-Molekel. Er wird als 10,10'-Biacridonyl vermutet. Die Geschwindigkeitskonstante der Primärreaktion wird zu $\approx 30\ \mathrm{Mol^{-1} \cdot s^{-1}}$ bestimmt.

Acridine derivatives constitute convenient model compounds for the investigation of bioluminescent reactions of some luciferins. As a result of their extensive studies on CL oxydation of acridan esters

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* Second part of a series of study on ozone induced chemiluminescence. The first part appeared in Z. physik. Chem. Neue Folge **96** (1975) 109.

and acridinium salts, McCAPRA et al. identified N-methylacridone as the emitting species, and postulated a dioxetane intermediate whose decomposition yields the required excitation energy [1].

On the other hand, it is interesting to find acridone (I) among the long list of compounds which give rise to luminescence upon reaction with ozone [2].

Even though ozone is not a natural constituent of bioorganisms, its strongly CL reaction with acridone, which is the parent compound of N-methylacridone seemed suitable for the study undertaken here, as a contribution towards the understanding of the reaction leading to bioluminescence.

From its stoichiometry and a preliminary analysis of the end-products, the reaction appears to be very complex. From its kinetic study, it was possible to arrive to a reaction scheme incorporating the main steps leading to CL and to propose a structure for one key intermediary.

Experimental

Reagent solutions were prepared from Acridone (Fluka) [recrystallised from ethanol-water (m.p. 354°)] and acetic 100% (Merck G.R.). All other solvents were Merck G.R. and were used without further purification. Ozone generation and preparation of its solutions in acetic acid as well as the CL recording set up were the same as described in a previous work [3], the only differences consisting in the use of a 1 cm quartz fluorescence cell for the reaction and the use of oxygen alone for ozone production. Phosphorescence spectra were recorded on a Hitachi Perkin Elmer MPF-2A spectrofluorimeter with its phosphoroscope attachment. Merck silicagel precoated plates were used for preparative TLC.

During all CL experiments as well as all the reactions in continous ozone flow the rate of gas flow was 30 ml $\cdot$ min^{-1} corresponding to an inflow of ozone of 2.5×10^{-8} mole $\cdot$ sec^{-1}, determined as described previously [3].

Results and discussion

Preliminary observations

When a stream of ozone containing oxygen is passed through a solution of acridone (I) in acetic acid, there is emission of strong blue luminescence. Fig. 1 a shows the evolution of CL spectra during
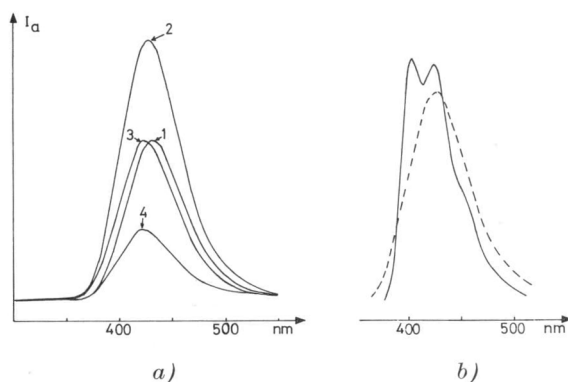
Fig. 1. *a)* Ozone-acridone CL emission spectra at various stages of reaction in acetic acid. *b)* Superimposed CL emission (– – –) and acridone fluorescence (———) spectra

a typical reaction where it can be noticed that the maximum shifts from 430 to 425 nm as the reaction draws to its end.

As seen in Fig. 1 b the CL maximum at 423—425 nm overlaps with the fluorescence of acridone even though lacking the more structured aspect of the latter. It seems then, that the recorded CL is due to production of excited singulet of acridone. The slight blue shift (≈ 5 nm) of the CL emission during reaction can thus be attributed to the disappearance of the inner filter effect of acridone along its consumption by ozone. From our determinations, the inner filter effect of acridone in acetic acid at 425 nm, is noticeable for concentrations above 4.1×10^{-5} M and a path length of 1 cm. During the recording of CL emission the effective thickness is reduced due to ozone bubbling and the critical concentration is at a higher value as seen later in the relationship between maximum CL intensity and initial acridone. Unfortunately, for concentrations of acridone where there is no inner filter effect, the CL signal was too weak to record sufficiently well defined spectra, in order to see if the blue shift still persists.

In the presence of acrylonitrile, the CL reaction is quenched since ozone preferentially reacts with this substance. As the amount of acrylonitrile in solution decreases the reaction with acridone becomes sufficiently competitive as evidenced by the appearance and increase of a CL signal. If acrylonitrile is added at the stage when the CL intensity has reached its maximum value, and ozone is cut-off, the CL
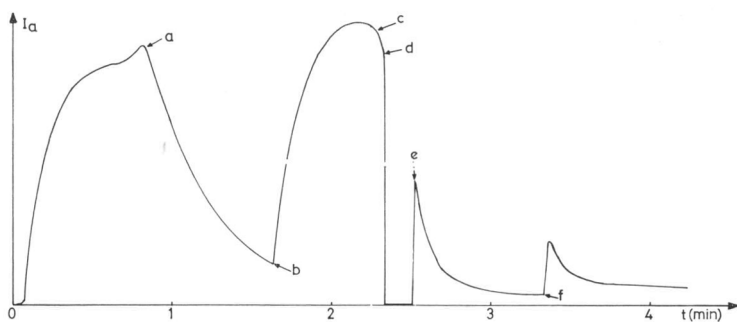
Fig. 2. Influence of acrylonitrile on CL emission at 425 nm v.s. time: *a)* normal CL decay upon ozone cut-off, without acrylonitrile addition; *b)* ozone ON; *c)* ozone OFF; *d)* shutter closed, acrylonitrile added; *e)* shutter opened; *f)* ozone ON
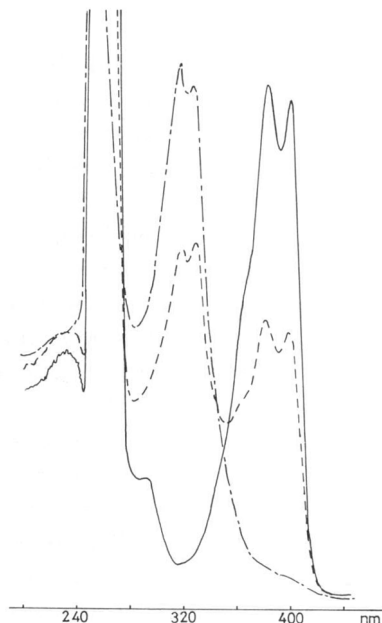

Fig. 3. Absorbance spectra of the reaction mixture at initial (———), inter-mediary (— — —) and final (—·—·—·) stages of CL emission

quenching due to the reaction with remaining ozone in solution can be noticed when compared to CL decay without the quencher (Fig. 2). Furthermore, when ozone is reintroduced there is emission of a CL

flash which can be interpreted as being due to reaction of an inter-
mediary product and ozone at a higher rate than the quenching reac-
tion (Fig. 2). The CL species is most likely not in its triplet state since,
if it were so, no CL would be observed in the presence of a triplet
quencher such as acrylonitrile assuming that quenching by oxygen
is not sufficiently efficient.

Absorbance spectra of the reaction mixture at various stages
(Fig. 3) shows the appearance of a peak with two maxima at 320 and
330 nm at the expense of the two main peaks of acridone at 382 and
398 nm, while the band at 260 nm is shifted to 250 nm. If ozonation
is continued past the end of CL emission, the absorbance at 320—
330 nm decreases as a consequence of the breakdown of the "primary"
end product. This species absorbing at 320 nm has a fluorescence at
374 nm (excitation 320 nm). Since there is a good overlap between
this fluorescence and the absorption spectrum of acridone (Fig. 4), it is
possible that the excited species formed by the CL step is this com-
pound in its S_1 state and that it transfers its energy to acridone which
emits the observed CL. The fluorscence at 374 nm is time dependent,
indicating that the CL species is of limited stability at room tempera-
ture in the presence of oxygen and light.

Phosphorescence spectra of the reaction mixture show a peak at
470 nm which increases as the reaction proceeds while the peak of
acridone at 520 nm decreases steadily (Fig. 5). Phosphorescence life-
times are approximately the same for acridone and the emission at
470 nm: $\tau_{1/2} \approx 1$ s at 77 K.

The CL intensity in acetic acid is several orders of magnitude
larger than in any other solvent tested (methanol, acetone, DMSO,
DMF). With the apparatus at hand, only in DMF, a very weak CL
could be detected. According to KOKUBUN's study on the electronic
spectra of acridone [4] it can be inferred that in acetic acid the neutral
form of the molecule is predominant so that the initial ozone attack
leading to CL must occur on this form. The same observation applies
to solvent acetone and since acridone fluorescence is the same both
in acetic and acetone, low efficiency of energy transfer from excited
CL species to acridone cannot account alone for the large difference
in CL intensity. Acetone may be thought of as interfering in a key
step of ozonolysis according to CRIEGEE mechanism, whereby it
combines with the zwitterion resulting from the dissociation of the
molozonide [5] thus implying this type of an intermediate on the CL
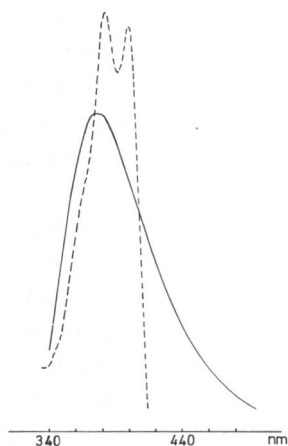reaction path.

Fig. 4. Fluorescence emission of the presumed CL species (———) superimposed to acridone absorbance (------) spectrum
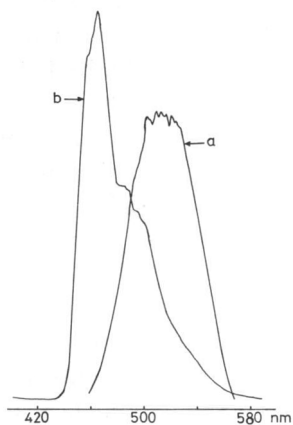

Fig. 5. Phosphorescence spectra at 77 K in acetic acid. *a)* Acridone; *b)* reaction mixture at the end of CL emission

When the ozone-acridone reaction was carried in preparative amounts, five blue-fluorescent compounds could be isolated by TLC (First, remaining acridone was removed by elution with chloroform-methanol 10:1 v/v. The blue spot corresponding to products was then separated with the same solvents in 1:1 v/v ratio.). Given the excessive ozonation required for this synthesis, some of these products must have appeared after the CL stage was over. The high stoichiometric
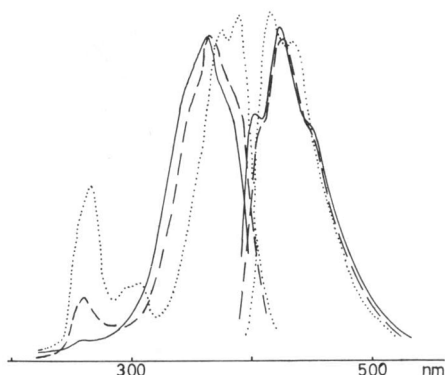
Fig. 6. Fluorescence excitation and emission spectra of three major compounds isolated at the end of extensive ozonation. (Solvent: acetic acid)

ratio of ozone to acridone (7 moles of ozone per mole of acridone, determined as described in our previous work [3]) can thus be attributed to the multiplicity of reaction steps leading to several products. As shown in Fig. 6, the fluorescence spectra of these products are very similar to acridone's. A tentative spectral differentiation by changing to a non-polar solvent (CCl_4) didn't give a significant variation.

With acridine (II) in acetic acid no CL could be detected and the reaction is much slower than with acridone. The same observation applies to xanthone (III) as well, showing the importance of the nitrogen in the ring for CL production.

Kinetics

The ozone—acridone reaction was studied kinetically with various relative amounts of the reactants. The experimental results could be specifically correlated with those calculated from a postulated reaction sequence.

Kinetics with continuous ozone flow

Acridone (4.1×10^{-5} M) decrease was monitored by fluorescence (exc. 396 nm, em. 425 nm) under a continous bubbling of ozone (30 ml $\cdot$ min^{-1} 2.5×10^{-8} mole $\cdot$ sec^{-1}). The interference of the CL emission on the fluorescence was entirely negligible at the sensitivity of measurement. In Table 1, the pseudo-first order rate constants calculated from experimental curves for two runs, show that for about $60^0/_0$ of initial acridone, the reaction proceeds as first order. This part
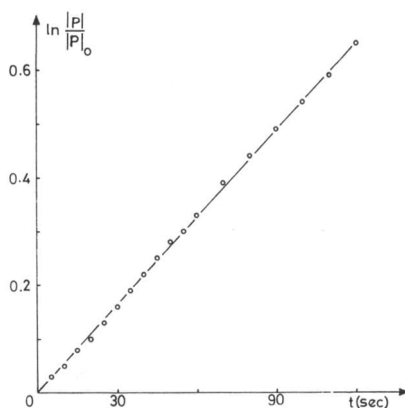
Fig. 7. Semi-logarithmic plot of product concentration (absorbance at 330 nm)
v.s. time

of the reaction corresponds to the initial increase and the maximum
plateau of CL. The final stages no longer satisfy the first order pattern
most likely due to competitive reaction paths of acridone with prod-
ucts of the initial reaction gaining importance.

In the same experimental conditions as above, the formation of
the product absorbing at 330 nm proceeds also as a pseudo-first order
reaction (Fig. 7).

CL curves at 425 nm with various initial acridone concentrations
show that the height of the CL plateau is directly proportional to

Table 1. *Pseudo-first order rate constants calculated from acridone fluorescence
decay curves under continuous ozone flow*

$[Acridone]_0 = 4.1 \times 10^{-5} M$, ozone: $30 \; ml \cdot min^{-1}$, $2.5 \times 10^{-8} \; mole \cdot sec^{-1}$

Time (s)	Pseudo-first order rate constant		Time (s)	Pseudo-first order rate constant	
	Expt. 1	Expt. 2		Expt. 1	Expt. 2
10	1.23×10^{-2}	1.21×10^{-2}	60	1.24×10^{-2}	1.24×10^{-2}
15	1.22	1.25	65	1.28	1.27
20	1.23	1.24	70	1.27	1.24
25	1.25	1.24	75	1.32	1.25
30	1.23	1.17	80	1.33	1.27
35	1.21	1.20	85	1.34	1.29
40	1.21	1.24	90	1.41	1.32
45	1.22	1.24	95	1.43	1.34
50	1.24	1.22	100	1.47	1.36
55	1.26	1.24	110	1.50	1.38
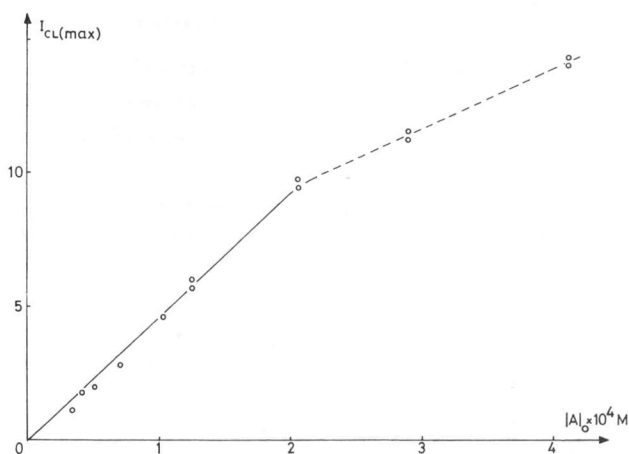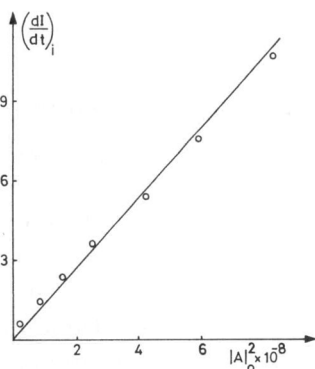
Fig. 8. *a)* Maximum CL intensity (arbitrary units) v.s. inital acridone con-
centration.   *b)* Initial slope of CL intensity v.s. the square of initial acridone
concentration

initial acridone within the limits where there is no inner filter effects
(Fig. 8 a). Note that the upper concentration limit is higher than the
one determined by fluorescence measurements because of the lowering
of the thickness by the gas bubbling through the solution.

Furthermore, from the same CL curves it appears that the initial
slope of CL emission is linearly related to the square of initial acridone
(Fig. 8 b).

Kinetics in excess acridone

When, in a given experiment, ozone is cut-off at the height of the CL plateau, the decrease of light emission that ensues is exponentially related to the time. The results of one such experiment are given in Table 2.

Table 2. CL *decay in excess acridone*
[Acridone]$_0$ = 4.1 × 10^{-5} M. (CL in arbitrary units)

Time (s)	ln CL	— k_{CL}	Time (s)	ln CL	— k_{CL}
0	4.91		45	3.58	2.9 × 10^{-2}
5	4.78	2.6 × 10^{-2}	50	3.47	2.9
10	4.62	2.9	55	3.33	2.9
15	4.50	2.7	60	3.22	2.8
20	4.33	2.9	65	3.04	2.9
25	4.17	2.9	70	2.94	2.8
30	4.01	3.0	80	2.64	2.8
35	3.89	2.9	90	2.20	3.0
40	3.74	2.9	100	2.08	2.8

Kinetics in near-stoichiometric conditions

In these experiments, solutions of ozone in acetic acid were mixed with solutions of acridone in the same solvent, and the reaction was followed by acridone absorbance at 398 nm. At the experimental conditions of this study (near-stoichiometric initial concentrations of reactants, T = 25°) the rate of reaction turns out to be dependent on the square of acridone concentration (Table 3 a, b).

The preceding experimental kinetic results can be summed up as: with constant ozone concentration (continous flow):

$$d[A]/dt = k_a[A] \tag{1}$$

$$I_{CL(max)} = k_{CL}[A]_0 \tag{2}$$

$$(dI_{CL}/dt)_{initial} = k[A]_0^2 \tag{3}$$

$$d[P]/dt = k_P[P] \tag{4}$$

with excess acridone:

$$I_{CL} = (I_{CL})_0 \exp(-kt) \tag{5}$$

at near-stoichiometric ratios of reactants:

$$d[A]/dt = k_s[A]^2. \tag{6}$$

In an attempt to arrive to an experimentally sound scheme as a primary guideline for future proposals of a reaction mechanism,

Table 3a. *Type I second order rate constants* for acridone decay in near-stoichio-metric conditions*

$[Acridone]_0 = 2.43 \times 10^{-5}$ M, $T = 25°$

| Time (s)	Expt. 1 D_{398}	$[OZ]_0 = 1.33 \times 10^{-4}$M $k_{II}(M^{-1} \cdot s^{-1})$	Expt. 2 D_{398}	$[OZ]_0 = 1.23 \times 10^{-4}$M $k_{II}(M^{-1} \cdot s^{-1})$
0	0.186		0.186	
60	0.154	142	0.159	116
90	0.142	142	0.148	117
120	0.132	140	0.140	113
150	0.122	144	0.130	118
180	0.114	145	0.124	114
210	0.108	142	0.118	113
240	0.102	141	0.112	113
270	0.096	143	0.108	110
300	0.092	140	0.102	113

* Calculated from:

$$k_{II} = \frac{\varepsilon_{398}}{t} \left(\frac{1}{D} - \frac{1}{D_0} \right)$$

where $\varepsilon_{398} = 7650$ as obtained from a calibration curve.

Table 3b. *Experimental mean values of second order rate constants with respect to acridone, for various initial ozone concentrations*

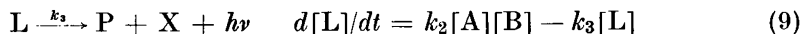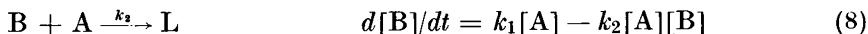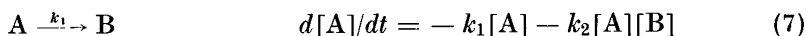| $[Ozone]_0$ (M)	$k_{II}(M^{-1} \cdot s^{-1})$
1.85×10^{-4}	177
1.38	154
1.33	142
1.28	132
1.23	114

several reaction sequences compatible with the preliminary observations were submitted to kinetic analysis. The following reaction sequence leads to analytical expressions satisfying simultaneously all the experimental kinetic results (1—6).

$$A + OZ \rightarrow B$$

$$B + A \rightarrow L$$

$$L + OZ \rightarrow P + X^*$$

$$X^* + A \rightarrow A^* + X$$

$$A^* \rightarrow A + h\nu.$$
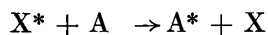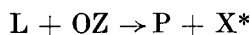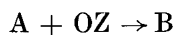
Thus, the reaction of intermediary B with acridone (A) produces species L which, in the preliminary experiments described, is responsible of the CL flash upon ozone reintroduction after quenching of the first step by acrylonitrile. P is the "end product" absorbing at 330 nm, while X* is the excited species which transfers its energy to acridone. Experimentally, the absorption at 320 nm with fluorescence at 374 nm, is attributed to X which reacts further and appears to be labile. The above reaction sequence is reduced to the main steps leading to CL; the various dark deactivation paths for X* as well as other possible dark reactions involving ozone are omitted.

The stoichiometry of 7 moles of ozone per mole of acridone and the multiplicity of "final compounds" found on ozonation past the end of CL emission, indicates that the total reaction is more complex than the postulated sequence. Nevertheless, since our kinetic experiments were not continued past the end of CL emission, the following reaction sequences where the latter stages are considered to be negligible, constitute a satisfactory basis for the mathematical analysis in order to see if the experimental kinetic behaviour is verified.

With constant ozone and considering the rate of energy transfer to be very fast relatively to the other steps, the reaction scheme takes the simplified form:

$$A \xrightarrow{k_1} B \qquad\qquad d[A]/dt = -k_1[A] - k_2[A][B] \qquad (7)$$

$$B + A \xrightarrow{k_2} L \qquad\qquad d[B]/dt = k_1[A] - k_2[A][B] \qquad (8)$$

$$L \xrightarrow{k_3} P + X + h\nu \quad d[L]/dt = k_2[A][B] - k_3[L] \qquad (9)$$

$$I_{CL} = k_3[L]. \qquad (10)$$

Assuming a steady state concentration for B, (8) yields:

$$[B] = k_1/k_2. \qquad (11)$$

Substituting (11) into (7):

$$d[A]/dt = -2\,k_1[A]$$

and

$$[A] = [A]_0 \exp(-2k_1 t) \qquad (12)$$

as observed experimentally (1).

At the maximum intensity of CL ($I_{CL(max)}$) (10) becomes:

$$I_{CL(max)} = k_3[L]_{max}. \qquad (13)$$

Since at this stage $dI_{CL}/dt = 0$, it results that $d[L]/dt = 0$ so that (9) gives $[L]_{max} = (k_2/k_3)[A][B]$ which is substituted in (13):

$$I_{CL(max)} = k_2[A][B]. \qquad (14)$$

Assuming a steady state concentration for B, (8) yields: $[B] = k_1/k_2$ and we arrive to:

$$I_{CL(max)} = k_1[A] = k_1[A]_0 \exp(-2k_1 t). \qquad (15)$$

Since, as observed experimentally, the time to reach the maximum CL is the same for a given ozone inflow, the exponential term in (15) is constant and in accord with experimental results we find that $I_{CL(max)}$ is linearly dependent on $[A]_0$ (2).

Differentiating (10) and substituting (9):

$$dI_{CL}/dt = k_2 k_3 [A][B] - k_3^2 [L]. \qquad (16)$$

Furthermore:

$$[A] = [A]_0 - \left([B] + [L] + \frac{[P]}{2} + \frac{[X]}{2}\right)$$

which at the very initial stages of the reaction approximates to:

$$[A]_i = [A]_0 - [B] \| \qquad (17)$$

(17) in (16) gives:

$$(dI_{CL}/dt)_i = k_2 k_3 ([A]_0 - [B]_i) [B]_i.$$

Since $[B]_i$ is very small we neglect the square term in $[B]_i$:

$$(dI_{CL}/dt)_i = k_2 k_3 [A]_0 [B]_i. \qquad (18)$$

Integration of (8) where [A] is substituted by (17) and the square term in $[B]_i$ is neglected, yields:

$$[B]_i = \frac{k_1 [A]_0}{k_1 + k_2 [A]_0} \{1 - \exp(-k_1 t - k_2 [A]_0 t)\}.$$

For t sufficiently close to zero, we approximate the exponential to the first two terms of its series expansion:

$$\exp\{-(k_1 + k_2[A]_0) t\} \approx 1 - (k_1 + k_2[A]_0 t)$$
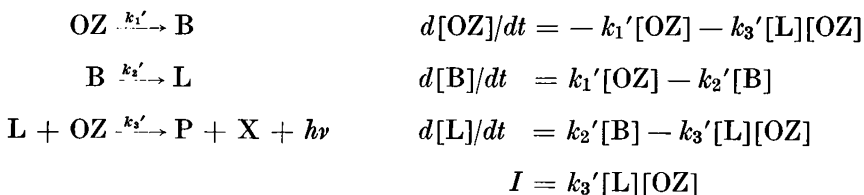
and arrive to:

$$[B]_i = k_1 [A]_0 t$$

which upon substitution in (18) gives:

$$(dI_{CL}/dt)_i = k_1 k_2 k_3 [A]_0^2 t$$

which is consistent with the experimental result (3).

In excess acridone the proposed reaction sequence reduces to:

$$\text{OZ} \xrightarrow{k_1'} \text{B} \qquad\qquad d[\text{OZ}]/dt = - k_1'[\text{OZ}] - k_3'[\text{L}][\text{OZ}]$$

$$\text{B} \xrightarrow{k_2'} \text{L} \qquad\qquad d[\text{B}]/dt\ = k_1'[\text{OZ}] - k_2'[\text{B}]$$

$$\text{L} + \text{OZ} \xrightarrow{k_3'} \text{P} + \text{X} + h\nu \qquad d[\text{L}]/dt\ = k_2'[\text{B}] - k_3'[\text{L}][\text{OZ}]$$

$$I = k_3'[\text{L}][\text{OZ}]$$

Since [B] and [L] are very small at all times we can assume a stationary concentration state and obtain:

$$[\text{B}] = (k_1'/k_2')[\text{OZ}]$$

$$[\text{L}] = k_1'/k_3'$$

and

$$I_{\text{CL}} = k_1'[\text{OZ}]$$

$$= k_1'[\text{OZ}]_0 \exp(-2k_1' t)$$

$$= (I_{\text{CL}})_0 \exp(-2k_1' t)$$

in accord with the experimental relation (5).

Finally, the fact that experimentally the reaction rate is first order for acridone in excess ozone and second order in near-stoichiometric conditions, is in accord with the mathematical treatment of type II second order reactions $\{-(d[\text{C}]/dt) = k[\text{C}][\text{D}]\}$ where the two reactants are in stoichiometric or near-stoichiometric concentrations, since it is shown that in such cases the integration of the rate expression leads to a result resembling that for a type I $\{-(d[\text{C}]/dt = k[\text{C}]^2\}$ second order reaction [6].

In the present case, where the stoichiometric ratio was found to be 7 moles of ozone per mole of acridone, if:

$$\Delta \leqslant [\text{A}]_0/4$$

where

$$\Delta = ([\text{OZ}]_0/7) - [\text{A}]_0$$

the analytical result would be:

$$(1/[\text{A}]') - (1/[\text{A}]_0') = 7\,kt\left(1 - \frac{\Delta^2}{4\,[\text{A}]_0'\,[\text{A}]_f'}\right)$$

where

$$[\text{A}]_{o,f}' = [\text{A}]_{o,f} + (\Delta/2) \qquad o:\ \text{initial}$$
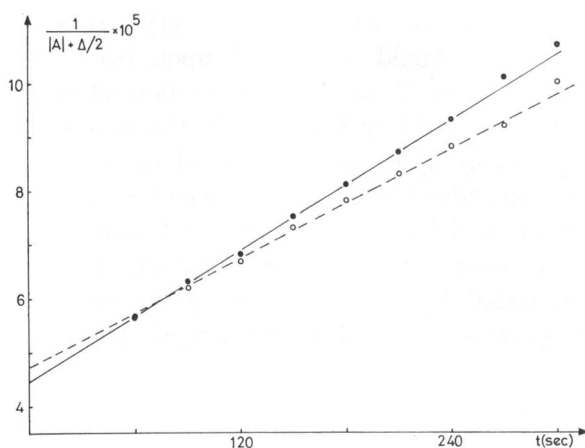
$$f:\ \text{final}.$$
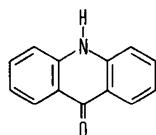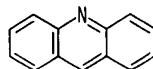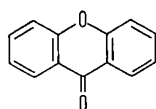
Fig. 9. $\dfrac{1}{[A] + [\varDelta/2]}$ v.s. time for two experiments. $[A]_0 = 2.43 \times 10^{-5}$ M
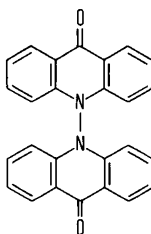(●): $[OZ]_0 = 1.33 \times 10^{-4}$ M; (○): $[OZ]_0 = 1.23 \times 10^{-4}$ M

(I) Acridone

(II) Acridine

(III) Xanthone

(IV) 10,10′ Biacridonyl

From the experimental conditions (Table 3a,b) it can be verified that $\varDelta$ falls within the limit for the above result to be applicable so that the rate appears to be second order in acridone.

With the experimental data of Table 3a the slopes of $(1/[A]')$ v.s. time for two experiments (Fig. 9) divided by $\left[7 \left(1 - \dfrac{\varDelta^2}{4[A]_0'[A]_f'} \right) \right]$ gives 32 and 28 M^{-1} · s^{-1} respectively for the actual second order rate constant.

From these results it is possible to postulate, as a starting point for further investigations, that the main CL reaction occurs via an

intermediary such as 10—10′ biacridonyl (IV), which according to our kinetic scheme, would be formed upon reaction of an initial oxidation product of acridone (B in the reaction scheme) with another acridone unit. 10—10′ biacridonyl (L in the reaction scheme) was synthesized originally by oxidation of acridone with chromic acid [7] and it is quite plausible that it is also formed by ozonation. Furthermore, this compound is known to be non-fluorescent and this is in accord with our own observations whereby the decrease of acridone is not accompanied by an immediate appearance of a noticeable fluorescence showing an evolution expected for a reacting intermediary.

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