# Spectra and Decay Kinetics of Diadamantyl-Dioxetane Chemiluminescence

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The thermal decomposition of 1,2-diadamantyldioxetane was studied by kinetic and spectroscopic methods. Spectra of the chemiluminescence emitted during the thermally induced decomposition of 1,2-diadamantyldioxetane, tetramethyldioxetane and trimethyldioxetane were obtained and the influence of quenchers and radical-scavengers, and the presence of "heavy atoms" in the surrounding of the emitting species was investigated. The kinetics of the decay mechanism was followed by measuring the time dependence of the chemiluminescence. The influence of radical-scavengers, quenchers and "external heavy atoms" on the kinetics was assessed. Experimental results were discussed in terms of a biradical decay mechanism.

The thermal decomposition of 1,2-dioxetanes produces chemiluminescence. The detailed reaction mechanism is still unclear. A concerted splitting of two bonds according to reaction scheme I can be reasonably explained by Woodward–Hoffmann-rules and by correlation diagrams similar to those for the thermal decomposition of cyclobutadiene [1].

Alternatively, the O–O-bond of the dioxetane can open first and the resulting 1,4-biradical decomposes to ketones by cleavage of the C–C-bond as shown in reaction scheme II:
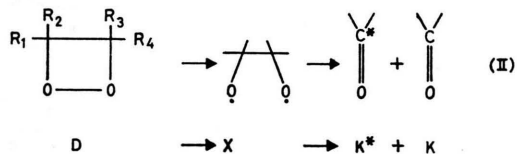
The conformation and electronic structure of the intermediate have been discussed in detail [2]. Two possible modes of excited-state production have

*Abbreviations:* CHL = Chemiluminescence; DAD = 3,4-diadamantyl-1,2-dioxetane; TMD = tetramethyldioxetane; TriMD = trimethyldioxetane; TTB = tri-*t*-butylphenole; EPA = ether-pentane-acetone mixture.

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been considered. X could be formed directly in the triplet state or, alternatively, X could be derived from a preceding singlet state via an "intersystem crossing" to the triplet state.

Mechanistic formulations must recognize that excited ketones are produced most favorably in the excited triplet-state [3], the yield of which depends on the dioxetane substituents. A distinction between the concerted and biradical pathways has not been experimentally feasible. ESR- und NMR-techniques lack the sensitivity to detect trace amounts of intermediates. The initiation of free-radical chain reactions cannot differentiate between the 1,4-biradical and an excited triplet carbonyl. The use of spin traps suffers from the same weakness. The kinetics of the decomposition of dioxetane and the decrease in their chemiluminescence is pseudo first order. This simple observed rate law does not distinguish between the proposed mechanistic alternatives. However, compounds which react with assumed intermediates or the final products can influence the observed kinetics. Oxygen has been used as a quencher for triplet states [4] and amines enhance the decomposition of 1,2-dioxetanes as well as metal ions [5]. By stepwise addition of quenchers and radical-scavengers to dioxetane solutions we have demonstrated that at least two different intermediates are attacked as could be shown by application of the Stern–Vollmer-equation [6]. Such an observation is inconsistent with a concerted reaction mechanism (scheme I). We have examined the influence of added quenchers and radical scavengers on the kinetics of the chemiluminescent decay and on the bands of the chemiluminescence spectra of diadamantyldioxetane (DAD) and other dioxetanes. Experimental results

were analyzed in the framework of the reaction mechanism presented in the theoretical part.
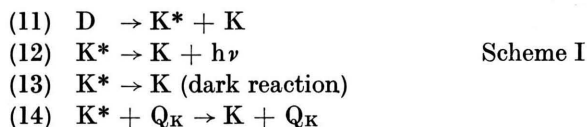
## Experimental

DAD was prepared by photooxydation of adamantylidenedadmantane [7]. The resulting dioxetane was chromatographed on a $SiO_2$-column in cyclohexane. The product thus obtained was adamantanone-free (no ketone absorption could be detected by UV: $\lambda_{max} = 260$ nm (49)). Gaschromatic analysis showed a single component ascribable to adamantanone. Adamantanone was prepared as described by Geluk et al. [8]. (IR: $\nu_{C=O} = 1690$ cm$^{-1}$, $\lambda_{max} = 280$ nm (n-heptane) (21)).

TMD was obtained according to Turro et al. [15]. TTB (Fluka, puriss.), 1,3-cis-pentadiene (Ferak), decaline (Eastman, spectrograde), bromobenzene (Fluka, puriss.), chlorobenzene (Merck, puriss.), acetone (Merck, Uvasol), n-heptane (Merck, Uvasol), n-pentane (Merck, Uvasol) were used without further purification.

Fluorescence measurements were made on a Farrand fluorimeter Mark I. 1 cm quartz cuvettes were used. In the concentration range investigated ($10^{-3}$ molar dioxetane) no correction for inner filter effects had to be applied. UV spectra were measured with a Cary 15, CHL spectra and measurement of the CHL-intensity integrated over the whole spectral range from 350–550 nm as a function of time were obtained as described earlier [6]. Degassed solutions were prepared by purifying solutions with nitrogen while measuring. Intensity measurements were made without addition of fluorescers in oxygen-free solutions, if not otherwise noted; $10^{-3}$ M DAD-solutions in decaline (spectrograde) were used.

## Theoretical Part

Dioxetane decomposition viewed as a concerted process can be described as follows:

(11)    $D \rightarrow K^* + K$
(12)    $K^* \rightarrow K + h\nu$         Scheme I
(13)    $K^* \rightarrow K$ (dark reaction)
(14)    $K^* + Q_K \rightarrow K + Q_K$

     (D = Dioxetane, K = Ketone,
     K* = excited Ketone, Q = Quencher)

Steady state approximations are valid because (11) is the rate-limiting reaction. The chemiluminescence intensity I is proportional to the number of photons produced per volume per second.

$$I \frac{d[h \cdot \nu]}{dt} = k_{12} \cdot [K] = \frac{k_{12}k_{11}[D]}{k_{12} + k_{13} + k_{14}[Q_K]} = \text{const}[D] \quad (1a)$$

Therefore, the rate of the decomposition of dioxetane is proportional to the rate of chemiluminescence decrease.

$$-\frac{dI}{dt} \sim -\frac{d[D]}{dt}$$

The time dependence of I is given by the integration of the first order differential equation for reaction (11) as:

$$[D] = [D_0] \cdot \exp(-k_{11}t) \quad (1b)$$

Inserting (1b) in equation (1a) and writing the first order rate law in logarithmic form one obtains:

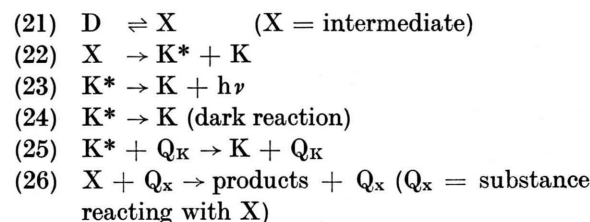$$\ln I = \text{const.} + \ln a - \beta t \quad (2)$$

where

$$a_1 = k_{11}k_{12}[D_0]/(k_{12} + k_{13} + k_{14}[Q_K]) \quad (3)$$
$$\beta_1 = k_{11} \quad (4)$$

The semilogarithmic plot of chemiluminescence intensity versus time according to (2) is a straight line with the same slope in the presence and absence of quenchers $Q_K$ as shown in Fig. 1 but the addition of $Q_K$ causes a drop. The decomposition of dioxetanes via intermediate(s) can be expressed as follows:

## Scheme II

(21)    $D \rightleftharpoons X$      (X = intermediate)
(22)    $X \rightarrow K^* + K$
(23)    $K^* \rightarrow K + h\nu$
(24)    $K^* \rightarrow K$ (dark reaction)
(25)    $K^* + Q_K \rightarrow K + Q_K$
(26)    $X + Q_x \rightarrow$ products $+ Q_x$ ($Q_x$ = substance reacting with X)

The scheme leads to:

$$I = k_{23}[K^*] = k_{23}k_{22}[X]/(k_{23} + k_{24} + k_{25}[Q_K]) \quad (5)$$

and

$$X = k_{21}[D]/(k_{-21} + k_{22} + k_{26}[Q_x]) \quad (6)$$

As in the previous Scheme I $dI/dt$ is proportional to $dD/dt$. If reaction (21) is reversible, then

$$-d[D]/dt = k_{21}[D] - k_{-21}[X] = \quad (7)$$
$$k_{21}[D](1 - k_{-21} + k_{22} + k_{26}[Q_x]).$$

Substituting (5) and (6) into (7) again an equation of type (2) is obtained,

$$\ln I = \text{const} + \ln a_2 - \beta_2 t \quad (2a)$$
$$a_2 = k_{21}k_{22}k_{23}[D_0]/$$
$$((k_{22} + k_{23} + k_{25}[Q_K]) \cdot (k_{-21} + k_{22} + k_{26}[Q_x])) \quad (8)$$
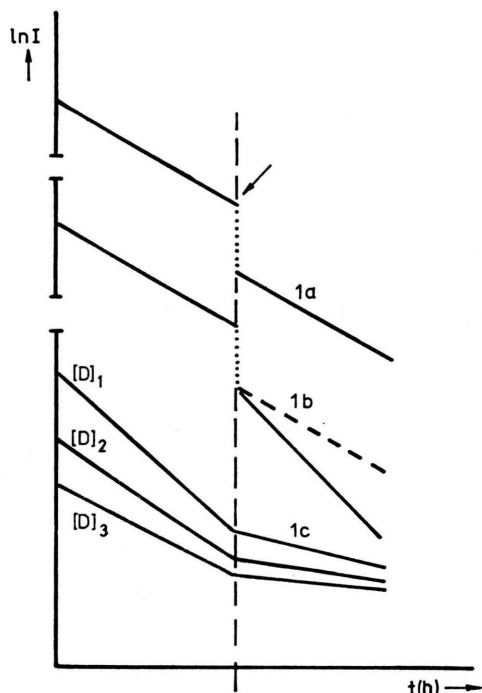$$\beta_2 = k_{21}(1 - k_{-21}/(k_{-21} + k_{22} + k_{26}[Q_x])) \quad (9)$$

Fig. 1. Influence of effectors on the CHL-decay curves of dioxetanes (semilog. plot). The arrow indicates the time of addition.

I a: Influence of a triplet quencher, concerted mechanism, scheme I.

I b: Influence of a triplet quencher $Q_k$ (dotted line) or a radical-scavenger $Q_x$ (straight line), biradicalic mechanism, scheme II.

I c: Influence of a triplet quencher $Q_K$ according to an autocatalyzed concerted mechanism, scheme III; the decay rate depends on the dioxetane concentration. $D_1 > D_2 > D_3$.

The semilogarithmic plot of this rate law is represented in Fig. 1 b. The influence of quenchers and scavengers can be easily demonstrated by equation (8) and (9). Addition of a quencher $Q_K$ has the same effect as in Scheme I, a decrease in $\ln I$ but no change of $d \ln I / dt$. In contrast the presence of the term $Q_X$ in $a_2$ and $\beta_2$ causes a decrease in $\ln I$ and an increase in $d \ln I / dt$ (cf. eq. (9)).

If no back reaction takes place ($k_{-21} = 0$) $a_1 = a_2$ and $\beta_1 = \beta_2$. The essential difference between the kinetics of scheme I and scheme II is this back reaction.

Scheme III

(31)  $D \rightarrow K^* + K$

(32)  $K^* \rightarrow K + h\nu$

(33)  $K^* \rightarrow K$ (dark reaction)

(34)  $K^* + Q_K \rightarrow K + Q_K$

(35)  $K^* + D \rightarrow$ products $+ Q_K$
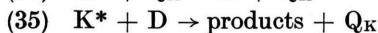
Turro et al. [7] have considered that $^3K^*$ may catalyze the decomposition of D. Previous work from our laboratory showed that the "catalyst" should be rather X than triplet-ketone [6].

Scheme III yields:

$$[K^*] = k_{11}[D]/(k_{12} + k_{13} + k_{14}[Q_K] + k_{35}[D]) \tag{10}$$

$$d[D]/dt = k_{11}[D] + k_{35}[D][K^*] = k_{11}[D](1 + k_{12}k_{35}[D])/ \tag{11}$$
$$(k_{12} + k_{13} + k_{14}[Q_K] + k_{35}[D]))$$

Expression (11) is a second order rate law in contrast to equation (2). The dependence of $d[D]/dt$ on $[D]$ and the retardation of the reaction rate by $Q_K$ is characteristic. This result is presented in Fig. 1 c.

Scheme IV

(41)  $D \rightleftharpoons X_1$

(42)  $X_1 \rightleftharpoons X_3$

(43)  $X_3 \rightarrow {}^3K^* + K$

(44)  $K^* \rightarrow K + h\nu$

(45)  $K^* \rightarrow K$ (dark reaction)

(46)  $K^* + Q_K \rightarrow K + Q_K$

(47)  $X_3 Q_X \rightarrow$ products $+ Q$

If more than one intermediate exists, scheme II must be extended. Several authors propose a mechanism with two sorts of biradicals, one with antiparallel and another with parallel spins of the lone electrons on the O-atoms which are characterized as singlet and triplet biradicals. The singlet state initially produced can undergo an intersystem crossing to the triplet state.

These considerations can be incorporated into the reaction scheme II by inserting (41), (42), (43). In the absence of back reactions the same expressions for $a$ and $\beta$ are obtained as in scheme I.

If (41) and (42) are reversible, new expressions must be derived:

$$a_4 = k_{43}k_{44}/(k_{44} + k_{45} + k_{46}[Q_K])(k'k''[D_0])/(1 - k'k''') \tag{13}$$
$$\beta_4 = k_{41} - k_{-41}k'' - k'k''k'''/(1 - k'k''') \tag{14}$$

with

$k' = k_{42}/(k_{-42} + k_{43} + k_{47}[Q_x])$

$k'' = k_{41}/(k_{-41} + k_{42})$

$k''' = k_{-42}/(k_{-41} + k_{42})$

The variation of $a_4$ and $\beta_4$ as a function of $Q_K$ is the same as in Schemes I–III. The influence of $Q_X$ on the kinetics is more difficult to discuss. An increase of $Q_X$ will result in a concomittant decrease of $(k'k'''/1-k'k''')$. Thus $Q_X$ causes a decrease of $a_4$ and an increase of $\beta_4$ (equations (13) and (14)). The influence of $Q_X$ will not be altered if $X_1$ reacts with $Q_X$ or if $X_1$ decomposes to $K^* + K$.

## Results

### Chemiluminescence spectra

The chemiluminescence spectra of DAD, TMD and TriMe D show the same emission band profile (see Fig. 2) with maxima at 405, 430, 475 and 525 nm. Bromobenzene enhances and $O_2$ and tri-$t$-butylphenole diminish the intensity of all spectral bands whereas 1,3-cyclohexadiene quenches the 475 band more than the other ones. For comparison the emission spectrum of photoexcited adamantanone, the final product of the DAD decomposition, is represented in Fig. 4.
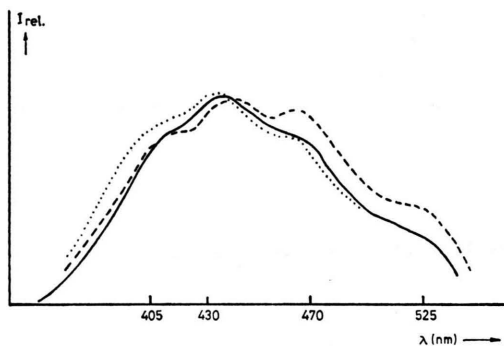


Fig. 2. CHL-spectra of DAD (straight line), TMD (puncted line) and TriMD (dotted line). $10^{-3}$ M solutions in decaline.

Nondeoxygenated adamantanone solutions in EPA show a fluorescence maximum at 410 nm. Bands at 430 and 475 nm appear only at temperatures about 77 °K in EPA. All these bands are visible in oxygen-free $n$-heptane solutions (see Fig. 3). Under these conditions, 1,3-pentadiene quenches the 430 and 475 nm band completely. These quenchings indicate that these bands arise from transitions of excited triplet states. The 475 nm band has been identified as a phosphorescence band of carbonyl compounds. The 430 nm bands has been similarly identified by some workers [9]. The different effects of the radical scavenger TTB and the triplet quencher 1,3-cyclohexadiene on these bands may suggest different assignments.
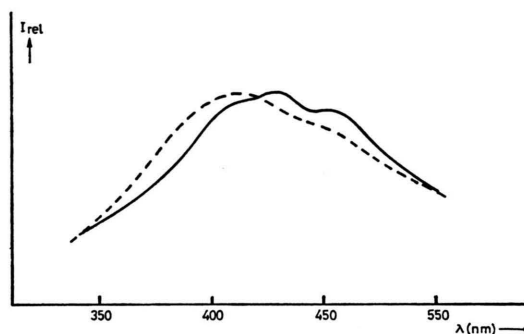


Fig. 3. Photoluminescence spectrum of adamantanone (straight line) $10^{-3}$ M solution in $n$-heptane. The like with addition of 1,3-pentadiene (dotted line).
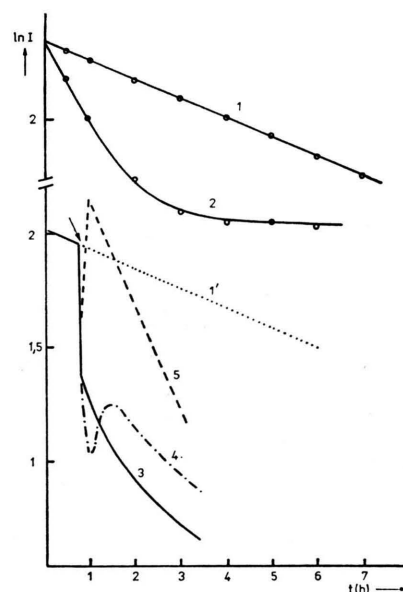


Fig. 4. CHL-intensity decay curves of DAD (semilog. plot).
1: $10^{-3}$ M solution in decaline at 121 °C, $N_2$ atmosphere.
1': The like ($N_2$ atmosphere) extrapolated if no effector would have been added.
2: The like, $O_2$ atmosphere.
3: At the arrow, addition of TTB ($N_2$ atmosphere).
4: At the arrow, addition of cyclohexadiene.
5: At the arrow, addition of bromobenzene.

### Kinetics

The time dependence of the DAD chemiluminescence intensity integrated over the whole spectral range of the emission in oxygen-free solutions is presented in Fig. 4. The linear semilogarithmic plot of I versus t indicates that the decay is first order. The slope is independent of the concentration of DAD. The presence of the decomposition product

adamantanone does not influence $I_0$ and the observed rate constant k. The values of k increase from $9.4 \cdot 10^{-6}$ s$^{-1}$ at 103.5 °C to 36 ($\pm 5$) $10^{-6}$ s$^{-1}$ at 125.4 °C.

The observed temperature dependence follows the Arrhenius equation and leads to an activation energy of $30 \pm 3$ kcal/mol ($125.4 \pm 12$ kJ/mol). A second activation energy can be calculated from the temperature dependence of $I_0$. A value of $35 \pm$ kcal/mol ($146 \pm 8.36$ kJ/mol) is obtained.

The difference of these two types of activation energy has been observed with other dioxetanes [10].

The luminescence decay of oxygen-containing solutions of DAD follows an entirely different course (Fig. 4, curve 2) which cannot be described by a simple kinetic law; a rapid initial decrease is followed by a very slow phase. This effect can be reversed by displacing the oxygen in the solution by nitrogen (Fig. 4). The effect of known triplet quenchers and radical scavengers on the decay of the integrated spectral intensity is also presented in Fig. 4, curves 3 and 4.

The radical scavenger TTB quenches the CHL intensity and accelerates the decay of DAD which must be due to a reaction with a radical intermediate because TTB is a very poor triplet quencher. Results with the triplet quencher 1,3-cyclohexadiene were qualitatively similar. Experimental difficulties due to the high volatility of this compound hindered a more quantitative analysis at the high temperatures necessary for DAD decomposition.

Addition of bromo- or iodobenzene to decomposing DAD solutions caused a higher CHL intensity and a more rapid decay velocity. The ln I *versus* t plot for bromobenzene containing solutions remained linear (Fig. 4, curve 5). We checked if the effect of bromobenzene might be due to an enhanced adamantanone emission, but we were not able to find any alterations of the ketone fluorescence spectrum in the presence of bromobenzene.

## Discussion

### a) Kinetics

The profiles of the experimental DAD chemiluminescence decay curves (Fig. 4) can be compared with the decay profiles derived from the various reaction mechanisms (1a–1c). Scheme I does not adequately describe the experimental results, be-

cause no quencher or radical scavenger lowers the luminescence intensity and simultaneously leaves the slope of the ln I/t curve unaltered. The triplet quencher 1,3-cyclohexadiene accelerates the chemiluminescent decay of DAD – as if a chain reaction took place besides the quenching effect of the diene. Similar results are found using TTB, which must react via a radical-like intermediate as described in eq. (26) or (6). The effect of bromobenzene on the chemiluminescence of the DAD decay can only be explained by the "external heavy atom effect". Singlet-triplet intersystem crossings are facilitated by this influence of heavy atoms. Bromobenzene must interact with a species other than $^1(n, \pi^*)$ ketone, because there was no effect on the fluorescence spectrum. We therefore suggest an intersystem crossing between two biradicals of singlet and triplet character which is followed or accompanied by a rotation to a sterical suitable position.
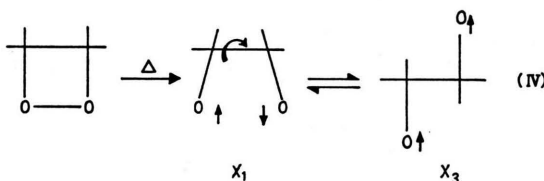


These processes have been incorporated into scheme IV by equations (42) and (−42). The reverse reaction $X_3 \rightarrow X_1$ (−42) could be evoked by additional rotational and vibrational energy quanta available at the temperatures of the experiment.

The effect of bromobenzene addition was computer simulated by variation of $k_{42}$ corresponding to an increase in reaction (42). That would simulate an increase of the local magnetic field in presence of the heavy atom favoring the singlet-triplet conversion. The simulation with an analog-computer follows exactly the course of curve 5, Fig. 4, if adequate values for the constants are chosen.

Qualitatively, the expression for $\alpha_4$ and $\beta_4$ increase with increasing $k_{42}$ assuming $k'k''' \ll 1$ and $k_{-41} \approx k_{42}$. An increase of $k_{42}$ rises the stationary concentration of $X_3$ enhancing the intensity produced *via* reactions (43) and (44). If stationary $X_1$ decreases by the external heavy atom effect less D is reformed by mechanism (−41) resulting in an increase of the overall rate $dD/dt$.

The influence of oxygen on the chemiluminescence decay curve of dioxetanes can be explained by formation of an oxygen-adduct, *e.g.* a cyclic

tetroxide [11]. Retardation of the CHL decay dioxetanes by $O_2$ is a general phenomenon that has been observed by other workers [12]. In the case of DAD decomposition we have resolved the fast phase of the very slow attainment of the biradical-tetroxide equilibrium in the case of DAD.

### b) Spectra

The precise nature of the light-emitting state may be deduced by inspection of the CHL-spectra and their modification by substances trapping or quenching intermediates. The CHL-spectrum of DAD, TriMeD and TMD exhibits in addition to the 405 nm band of the ketone fluorescence two other bands which must originate from triplet states. The temperature dependence of corresponding ketone bands, the oxygen sensitivity of the DAD-spectrum and the observed quenching by dienes are characteristic for phosphorescence. Two explanations could be given for the occurrence of two triplet bands:

1. The 430 and 465 nm bands originate from the same electronic state, but from different vibrational levels. The vibrational levels of the $C=O$ chromophore for ketones are known and have values of about 0.12 eV [13]. The energy difference between the two bands corresponding to $0.22 \pm 0.05$ eV is too large to be explained by the foregoing rationale.

2. The 430 nm band corresponds to the $^3(\pi, \pi^*)$-state and the 475 nm band to the $^3(n, \pi^*)$-state of the ketone [14]. The formation of triplet excimers being responsible for the 430 nm emission must be excluded because no concentration dependence of the relative band intensities for the 430 nm band in the ketone photoluminescence spectrum could be detected. So the dioxetane CHL-spectrum shows essentially the same bands as the previous adamantanone photoluminescence spectrum but with different relative band intensities. The enhanced intensity of these bands in the CHL-spectra is due to the favored production of triplet states during the decomposition process [1]. Turro found a relation of 10:1 triplet- to singlet-ketone for DAD. Values up to 100:1 are reported for other dioxetanes [15]. The dioxetane spectra possess an additional band at 525 nm which is not observed in the adamantanone spectrum. This band seems to originate from a species with a rather short lifetime because it is influenced by quenchers only to a small extent. It could be assigned either to a diketone band like that

observed after a long illumination of acetone [16] or to an electronic transition of a biradical intermediate which might also be accompanied by light emission. A CHL of biradicals produced by oxidation of dibenzopinakon-ketyl and by dibenzopinakolate have been observed at 570 nm [17]; a band at 525 nm has been found during the reaction of oxalic esters with $H_2O_2$ and been ascribed to the decomposition of dioxetanedione or one of its biradicalic intermediate products [18].

### c) Reaction mechanism

Scheme IV is the most satisfying model especially with respect to the influence of quenchers and trapping agents. The outstanding feature of Scheme IV is the introduction of an intersystem crossing from a singlet to a triplet state of the intermediate X. This addition to the reaction scheme accounts for the effect to the bromobenzene. Identifying $X_1$ as a biradical with anti-parallel spins of the "lone electrons" of the oxygens and $X_3$ as a biradical having parallel spins, the formation of singlet and triplet states of ketone can be formulated as follows:
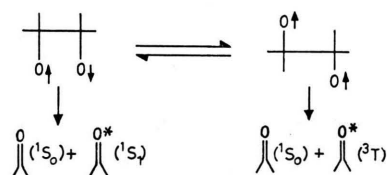


Scheme IV should be expanded to explain the production of different spin isomers of excited ketones from biradicals:

(41)    $D \rightleftharpoons X_1$

(42)    $X_1 \rightleftharpoons X_3$

(43a)    $X_3 \rightarrow {}^3K^* + K$

(43b)    $X_1 \rightarrow {}^1K^* + K$
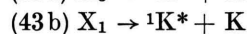
The ratio $^1K^* : {}^3K^*$ is determined by the transformation of $X_1$ into $X_3$ and $^1K^*$ described by reaction steps (42) and (43). (42) is an intersystem-crossing process and should be greatly favored by rotation of the $C=O$ groups around the C–C-bond [18], therefore, dioxetanes with small substituents and stable C–C-bond should have a higher triplet yield whereas dioxetanes with an unstable C–C-bond should have a higher singlet yield (e.g., TMD, 100:1 [19]), tetramethoxydioxetane, 10:1 [19]) because of the electron-withdrawing methoxy

groups which weaken the C–C-bond. The observed ratio of 10:1 at the DAD–CHL should be caused by the bulky adamantyl groups which induce a strain on the central C–C-bond. Therefore, $k_{42}$ should be of the same order of magnitude as the corresponding constant for 1,4-dienes, $e.g.$ $10^7$ $s^{-1}$. According to our kinetic model the triplet-singlet yield is determined by the expression (assuming stationary states):

$$[X_3]/[X_1] = k_{42}/(k_{-42}+k_{43b}).$$

The variation of triplet yields the individual values of $k_{43b}$. Reactions (43a) and (43b) include the cleavage of a C–C-bond with an activation energy of about 11 kcal/mol as estimated by O'Neal and Richardson [18]. According to MO-theory the first
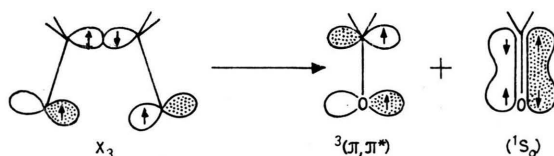


product of the C–C-split in $X_3$ should be the $^3(\pi, \pi^*)$ ketone.

Therefore, the transition $^3(\pi, \pi^*) \rightarrow {}^1S_0$ should be responsible for the 430 nm band whereas the 475 nm band should be caused by the transition $^3(n, \pi^*) \rightarrow {}^1S_0$. The spatially forbidden radiationless transition from $^3(\pi, \pi^*) \rightsquigarrow {}^3(n, \pi^*)$ is facilitated by vibrational and rotational perturbations of the molecule symmetry.

## Conclusion

The communicated results of the kinetic and spectroscopic investigations of the chemiluminescence of DAD, TriMD and TMD are best understood by postulating the existence of biradicalic intermediates in the thermal decomposition of dioxetanes. The hypothesis of a concerted cleavage is inadequate to account for our observations.

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