165. Thermolysis and Chemiluminescence of Monocyclic 1,2,4-Trioxan-5-ones

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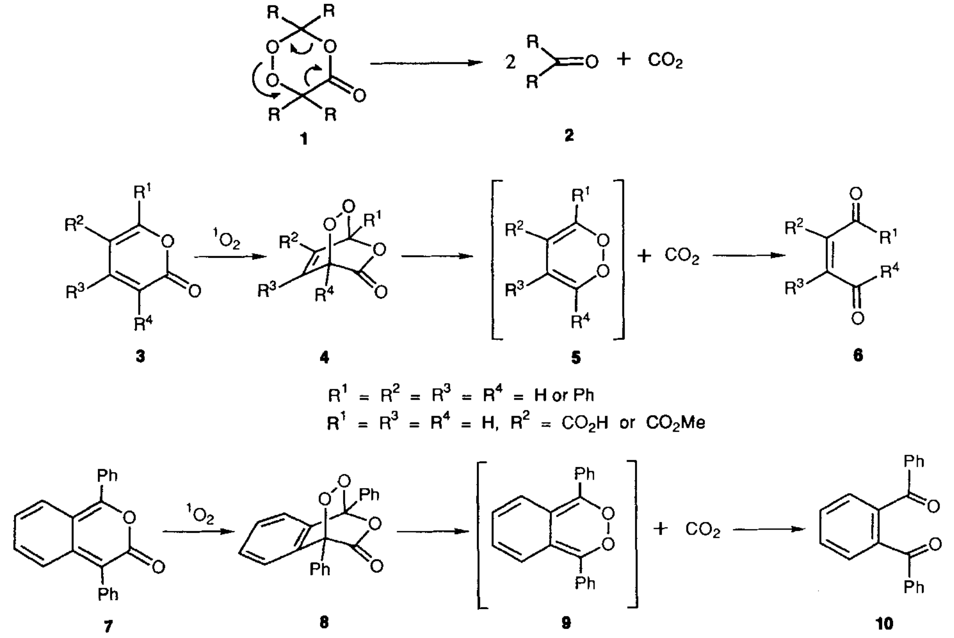
The 3,6-substituted 1,2,4-trioxan-5-ones **11**–**14**, on heating to 170–200°, underwent unimolecular thermolysis to generate electronically excited singlet ketones with an efficiency of *ca.* 0.2%. The chemiluminescence quantum yields (ϕ_{CL}) depended on the nature of the 6-substituents and increased linearly with temperature. The *Arrhenius* activation energies were obtained by measuring the rate of decay of luminescence and determined as 22.9, 30.4, 35.6, and 34.2 kcal/mol for **11**–**14**, respectively. Step analysis of the chemiluminescence of **14** afforded an average activation energy of 44.3 kcal/mol. This latter result is explicable in terms of two decomposition paths, higher and lower in energy, leading to excited and 'dark' products, respectively. The thermolysis of trioxanones **12**–**14** lacking a H-atom at the 6-position is interpreted as involving successive rupture of the peroxide bond, excision of ketone at the 3-substituted end, and loss of CO_2, to finally produce ketone originating from the 6-position (see *Scheme 4*).

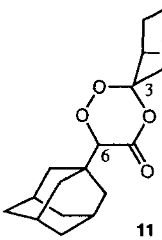
Introduction. – Until recent times, few 1,2,4-trioxan-5-ones (**1**) have been prepared. They are essentially unknown as a chemical class. Chemists have instinctively believed that they would be intrinsically unstable. Fragmentation of **1** to CO_2 and two molecules of ketone **2** was thought to be an easy, perhaps spontaneous process (*Scheme 1*) [1].

Scheme 1



Indeed, the bridged bicyclic trioxanones **4**, obtained by dye-sensitized photooxygenation of the 2*H*-pyran-2-ones **3**, underwent decarboxylation to the ene-diones **6** at room temperature. There was no evidence for the intermediate 1,4-dioxin **5** (*Scheme 1*). Light was also emitted, but of very low intensity [2]. In contrast, the related benzo-annelated 1,2,4-trioxanone **8** was isolated as a stable, crystalline solid after photooxygenation of 1,4-diphenyl-3*H*-2-benzopyran-3-one (**7**) [3] [4]. Heating at 92° was required to decompose **8**, which occurred without any detectable luminescence (*Scheme 1*). As before, decarboxylation was the main event giving initially *o*-xylylene peroxide **9** and then diketone **10**. When both experiments were repeated in the presence of an electron donor such as rubrene, luminescence was enhanced as fluorescence. The acceptor in the electron-exchange process was deduced as the trioxanone ring itself for the less stable trioxanone **4** and the peroxide **9** for the more stable trioxanone **8**. Consequently, light emission may not be a characteristic of stable trioxanones, especially if an intermediate is produced on thermolysis.

In order to address this fundamental question, we now describe a study of the thermolysis and direct chemiluminescence of the 3,6-substituted monocyclic 1,2,4-trioxan-5-ones **11**–**14** where the formation of intermediate cyclic peroxides is excluded.



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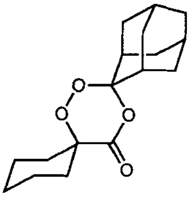

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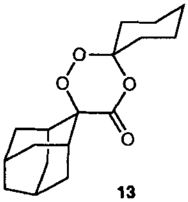

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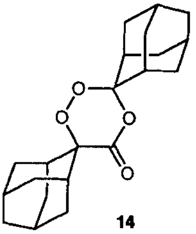

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Experimental. – Samples of trioxanones **11**–**14** were prepared [5] and examined as aerated solns. in 1-phenyldecane at concentrations in the mmol range. Owing to their remarkable thermal stability [6], luminescence measurements were performed at high temperatures (170–220°). Accordingly, solns. of the sample were heated in a home-made furnace consisting of a block of Al hollowed out to receive a quartz cuvette and provided with a window permitting light to escape and be detected (*Fig. 2*). The block was suspended by three screws inside a protective cylindrical casing. The block was heated electrically and the temp. of the sample determined by a digital thermometer which was calibrated against a conventional Hg thermometer. Agreement between the two was within 2°. The light produced by thermolysis of the sample was collected and focused by a lens into a beam which was interrupted by a chopper and then refocused on a photomultiplier tube by a second lens (*Fig. 2*). The set-up was controlled by a lock-in amplifier and data acquired by using home-made interface equipment and an *AT* personal computer.

Results. – *Activation Energies.* Individual samples of trioxanones **11**–**14** were heated at different fixed temperatures. In each case, the decrease of the resulting intensity of chemiluminescence was measured as a function of time. All, except **12** which presented slight deviations, underwent exponential decay at constant temperature consistent with unimolecular decomposition. Typically, the decay of luminescence was long; trioxanone **13** in 1-phenyldecane as solvent at 220° took more than 1 h for complete extinction

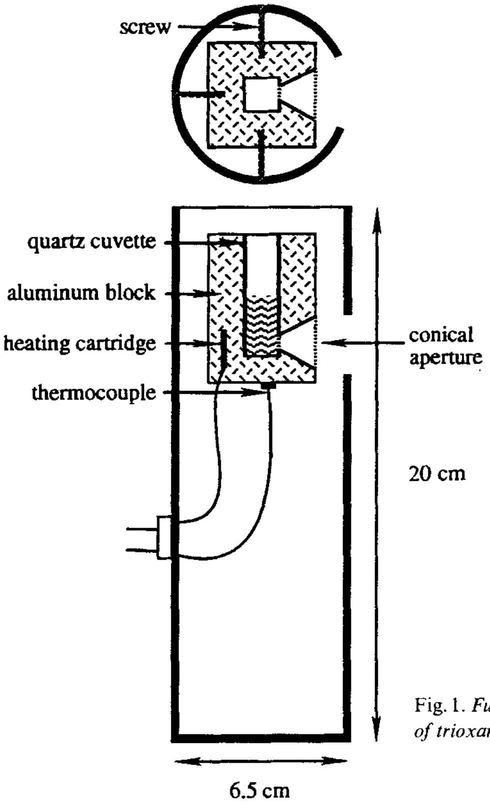


Fig. 1. *Furnace for heating solutions of trioxanones*

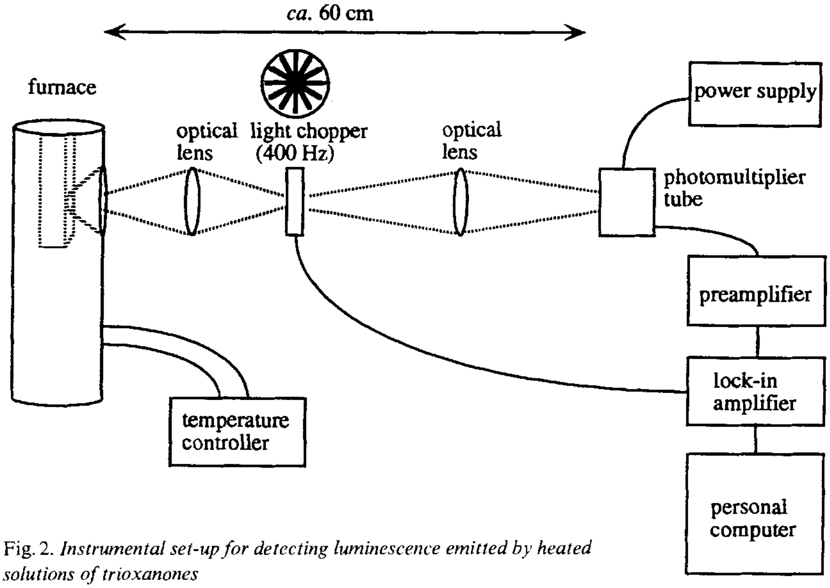


Fig. 2. *Instrumental set-up for detecting luminescence emitted by heated solutions of trioxanones*

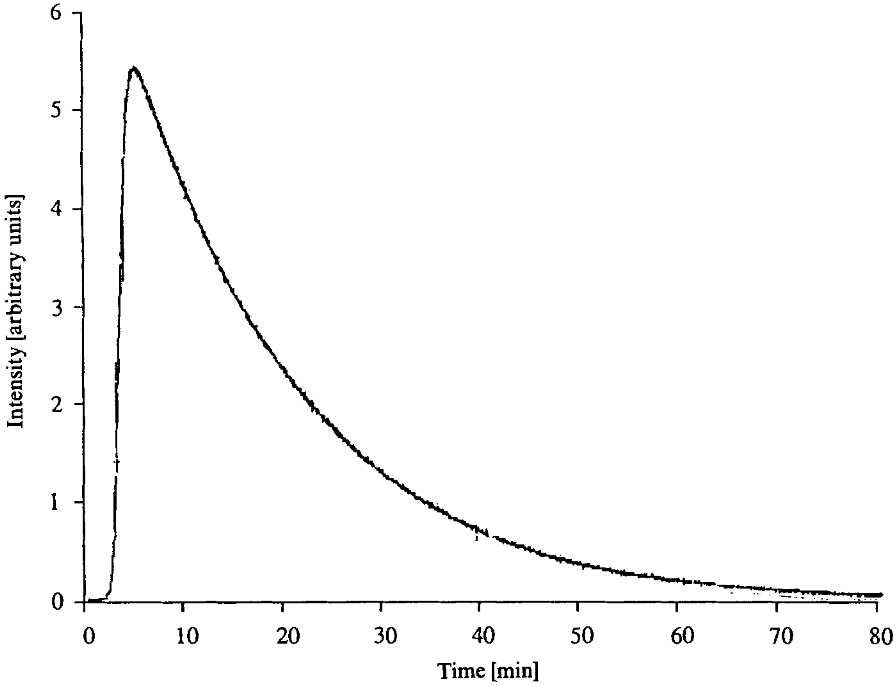


Fig. 3. *Observed chemiluminescence as a function of time for trioxanone* **13** *in 1-phenyldecane at 220°*

(*Fig. 3*). The light intensity (I) is determined by the rate of thermolysis of the trioxanone into the fragments A*, B, and C (slow step) and the efficiency of chemiluminescence (CL) of the light-emitting species A^* so produced in the fast step (*Scheme 2*). The kinetic equation relates I to the quantum yield of CL, ϕ_{CL} or the number of photons produced per number of molecules decomposed, and to the rate constant observed (k_{obs}) for the first or slow step of reaction (*Eqn. 1*). By measuring the rate of decay at different temperatures and plotting $\ln k_{obs}$ so obtained against the reciprocal of the temperature ($1/T$), a straight line was obtained for all four trioxanones (*Eqn. 2*). The *Arrhenius* parameters, namely the activation energies (E_a) and the pre-exponential term A, were extracted by standard analysis (*Table 1*). Trioxanone **12** gave a larger confidence interval, since its decay departed slightly from that of a simple exponential.

Scheme 2

$$\text{trioxanone} \xrightarrow[\substack{\text{slow step}\\ k_{obs}}]{\Delta} \mathrm{A^* + B + C} \xrightarrow[\text{fast step}]{} \mathrm{A + B + C} + h\nu$$

$$I = \Phi_{CL}\frac{d[A^*]}{dt} = \Phi_{CL}\,k_{obs}\,[\text{trioxanone}] \qquad (1)$$

$$k_{obs} = A\exp(-E_a/RT) \qquad (2)$$

$$I = C\exp(-E_{CL}/RT) \qquad (3)$$

Table 1. Arrhenius *Parameters Determined for Trioxanones* **11–14**

	Activation energy E_a [kcal/mol]	$\log A$
11	22.9 ± 3.25	7.3 ± 0.2
12	30.4 ± 4.3	11.0 ± 0.2
13	35.6 ± 1.8	12.9 ± 0.2
14	34.2 ± 1.6	13.0 ± 0.2

Trioxanone **14** was further examined by the temperature-step method [7] [8]. A sample was heated progressively and quickly in steps of 5° from 170 to 195°. After each stepwise increase, the temperature was held constant just long enough for the recorded signal of the luminescence to become stabilized (typically 3–5 min). At each temperature plateau, the initial instantaneous intensity of luminescence was measured. After reaching 195°, heating was decreased in the reverse order according to the previous procedure. At each descending step, the intensity of the corresponding luminescence was measured. Ideally, the concentration of the trioxanone solution remains unchanged during the incremental increase or decrease of temperature. Thus, the ratio of the intensities observed at each pair of temperatures equals the ratio of the corresponding observed rate constants, provided that ϕ_{CL} remains constant. In this instance, *Eqn. 3* applies. The constant C is characteristic of the instrumental setup. By plotting $\ln I$ against $1/T$, a straight line was obtained, so yielding E_{CL}, the activation energy for that fraction of the reaction leading to chemiluminescence. From the heating and cooling data, values of 40.1 ± 0.9 and 47.9 ± 0.7 kcal/mol were found, respectively. Partial decomposition undoubtedly accounts for most of this discrepancy and can be compensated for by taking the average value of 44.3 kcal/mol.

This latter value exceeds that found by the first method, because it was subsequently discovered, contrary to our assumption, that ϕ_{CL} is not independent of temperature. Measurement of this latter relation (*vide infra*) enabled the intensity changes to be adjusted for this temperature effect, thereby giving a rectified activation energy of 34.4 kcal/mol, in close agreement with E_a, the *Arrhenius* value.

Solvent Effects. Next, the influence of the nature of the solvent on the decomposition of **14** was investigated. Experiments carried out at 190° showed that decomposition in dimethyl sulfoxide ($k_{obs} = -5.9 \cdot 10^{-3}$ s^{-1}) was some 10 times faster than in 1-phenyldecane ($k_{obs} = -5.5 \cdot 10^{-4}$ s^{-1}), but with an integrated light intensity 6 times lower. The use of triethylene glycol dimethyl ether as solvent retarded decomposition by 30% ($k_{obs} = -7.2 \cdot 10^{-4}$ s^{-1}) without appreciably altering the light yield.

Singlet and Triplet Species. Attempts were made to determine the ratio of the concentration of singlet to triplet excited products by adding varying amounts of 9,10-dibromoanthracene (DBA) and 9,10-diphenylanthracene (DPA). DPA undergoes exclusively singlet-singlet energy transfer, while DBA is characterized by triplet-singlet energy transfer converting usually unobserved excited triplet ketone energy into light. The ratio of the observed light intensities at infinite concentration of either added DPA or DBA would permit the determination of the ratio of the concentrations of singlet to triplet excited cleavage products [9].

Previous flash-vacuum thermolysis studies [6] have shown that these trioxanones decompose into CO_2 and two carbonyl fragments. In principle, any of them could be produced in an electronically excited state. However, for trioxanones **12**–**14**, the light emitted presumably originates from the decay of singlet excited adamantan-2-one or cyclohexanone (*vide infra*). Since both of these molecules have a very low fluorescence quantum yield, energy transfer to a fluorescent acceptor would be expected to dramatically increase the light output. Samples containing trioxanone **13** (4.41 mM) and DPA (0 to 3.13 mM) at 190° were monitored. The rate of decay was found to be independent of the DPA concentration, a result consistent with the role of DPA as an energy acceptor. The light intensity increased with DPA concentration and furnished a straight line, when the reciprocal of the intensity was plotted against the reciprocal of the concentration of DPA. Extrapolation to infinite DPA concentration showed that DPA intensified fluorescence 60-fold.

Similar experiments were performed with added DBA. The rate of decay of fluorescence increased with greater concentrations but deviated from first-order, indicative of a more complex reaction. Moreover, light intensity increased only marginally as a function fluorescer concentration thereby revealing that little triplet excited ketone was produced.

Chemiluminescence Quantum Yields (ϕ_{CL}). Carefully weighed samples of trioxanones **11**–**14** in aerated 1-phenyldecane were heated at 200° and allowed to decompose completely, while the total luminescence emission was recorded. Data were converted to photon counts and subsequently expressed as ϕ_{CL} values (*Table 2*) by calibrating the light recorder with a standard aqueous solution of luminol, the oxidation of which generates a known number of photons [10].

Table 2. *Chemiluminescence Quantum Yields* (ϕ_{CL}) *of Trioxanones* **11**–**14**

11	$1.7 \cdot 10^{-7}$	**13**	$1.1 \cdot 10^{-5}$
12	$3.1 \cdot 10^{-7}$	**14**	$9.4 \cdot 10^{-6}$

It was further found that ϕ_{CL} increased with temperature for all trioxanones studied. The behavior of **14** was typical (*Fig. 4*). The spectral composition of the emitted light was investigated with the aid of three optical bandpass filters covering the regions 330–400 nm, 400–500 nm, and above 500 nm. Almost 90% of the light normally emitted was found to lie in the middle region, with 10% above 500 nm and even less below 400 nm. Experiments performed at 185–215° with the 400–500 nm bandpass filter in place showed that the integrated intensity still increased with temperature (*Fig. 4*). The difference in absolute quantum yields is an artefact and arose, because the collimating lens had to be moved slightly to accommodate the filter.

Effect of Oxygen. As molecular oxygen efficiently quenches triplets [7] and can also react with radicals [11], it was necessary to check its possible effect on luminescence. Two samples of trioxanone **14** in 1-phenyldecane were saturated respectively with O_2 and Ar and subsequently examined. Both samples gave the same integrated intensity and decay rate.

Discussion. – The first-order kinetics observed for the decay of luminescence confirms that fragmentation, exemplified by that of **13**, is a unimolecular process giving CO_2, cyclohexanone (**15**), and adamantan-2-one (**16**; *Scheme 3*). **14** yields in the same reaction CO_2 and two molecules of **16**. From a consideration of the energetics, CO_2 can be ruled out as an excited species in favor of **15** or **16**. The fluorescence spectra of **15** and **16** show

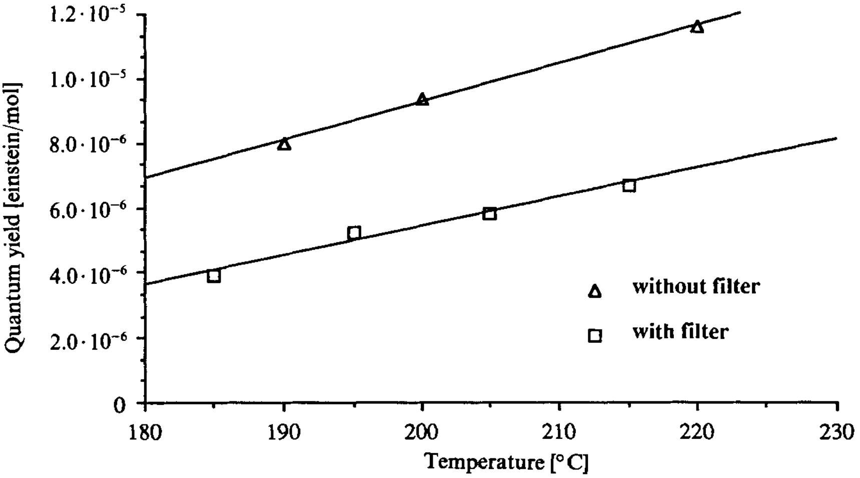


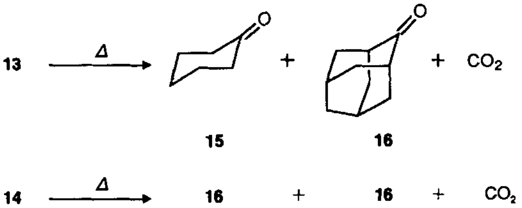
Fig. 4. *Integrated total chemiluminescence intensity as a function of temperature for trioxanone* **14** *at constant initial concentration with and without a 400–500-nm bandpass filter.* The estimated experimental error for each datum point is within 10%.

maxima at 405 and 420 nm, respectively, at 300 K in cyclohexane. CO_2 could also emit in this spectral region, but as its absorption spectrum lies below 200 nm, more energy would be needed to electronically excite CO_2 than the ketones [12] [13]. Information on the energy available was provided by a PM3 calculation [14] on a model compound, 3,3,6,6-tetramethyl-1,2,4-trioxan-5-one. The enthalpy of decomposition to CO_2 and two acetone molecules was evaluated as −68.2 kcal/mol. The addition of this value to the activation energy for **14**, namely 34.2 kcal/mol, furnishes 102.4 kcal in all. This energy corresponds to a photon having a wavelength of 279 nm, which is insufficient to excite electronically the CO_2 molecule. The filter experiments also confirm that the emission observed comes from excited ketones.

The observed sizable increase in intensity of emitted light on adding DPA confirms that decomposition produces singlet excited states. Although the triplet to singlet ratio could not be ascertained, the negligible increase in light intensity emitted in the presence of DBA certainly suggests that few triplet excited molecules are formed. Thus, assuming that the emission is caused by the excited ketones, the yield of the excited singlet states generated may be estimated by dividing the observed photon yield (*ca.* 10^{-5} einstein/mol for trioxanone **14**) by the fluorescence quantum yield of the ketone. For **16**, the emission observed at 420 nm has a fluorescence yield of $1.5 \cdot 10^{-2}$ in MeCN [15] and *ca.* $5 \cdot 10^{-3}$ in cyclohexane [16], both of which are independent of temperature [17]. By using this last value, which is appropriate for 1-phenyldecane, a value of *ca.* $2 \cdot 10^{-3}$ is obtained for the yield of electronically excited singlet ketones. This efficiency is, of course, remarkably low and means that nearly all (99.8%) of the adamantan-2-one produced is in the electronic ground state. This result may be compared with that of 4,4-dimethyl-1,2-dioxetan-3-one [18] [19]. Its thermolysis occurs more easily, at 30°, and produces excited acetone, some as singlet, but most as triplet, in efficiencies of 0.1 and 1.5%, respectively.

In another respect, the thermal behavior of the 4,4-dimethyl-1,2-dioxetan-3-one is relevant to that of **14**, namely the finding that E_{CL} is greater than E_a by 3–4 kcal/mol [18]. This difference was taken as evidence for decomposition proceeding by two competing pathways, one higher, the other lower in energy, leading to excited states and 'dark' products, respectively. Later, however, it was argued that the difference was merely due to partial decomposition occurring during the temperature-step experiment [19]. The case of **14** is unequivocal; E_{CL} exceeds E_a by *ca.* 10 kcal/mol, *after* allowing for decomposition. Moreover, ϕ_{CL} actually increases with temperature. It is therefore seen that the dual pathway mechanism is vindicated.

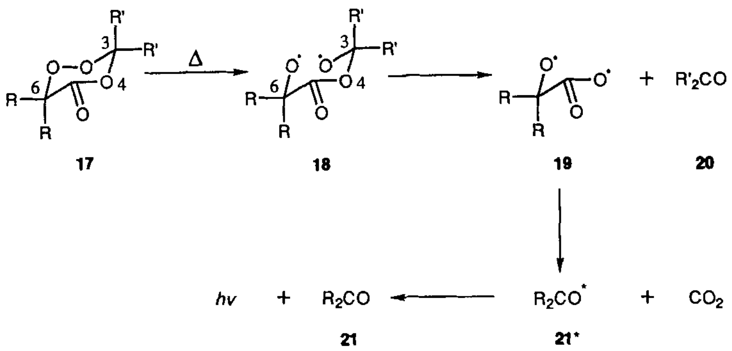
Scheme 3



Comparison of ϕ_{CL} for the trioxanones (*Table 2*) suggests that the emissive ketone originates solely from the C-atom α to the carbonyl group (C(6) position). The light efficiencies of **13** and **14** are the same within experimental error. The C(3) substituents are different, but both molecules possess a latent molecule of adamantan-2-one at the C(6) position, which on decomposition, produces the same excited species. The trioxanone **12**, which is isomeric with **13**, also contains a latent adamantan-2-one, but located at the C(3) position. However, **12** has a far lower light efficiency because excited cyclohexanone, excised at the C(6) site, has a lower fluorescence quantum yield than that of adamantan-2-one [20].

The foregoing trends provide a clue to the mechanism of thermal decomposition. The fact that **12** and **13** have substantially different quantum yields precludes a concerted, pericyclic reaction for decomposition, since both would produce the same excited fragments. Consequently, a stepwise process is more plausible (*Scheme 4*). The first event is

Scheme 4



homolytic rupture of the peroxide bond of **17**. The resulting singlet species **18** then eliminates a non-excited ketone **20** by selective cleavage of the C(3)–O(4) bond to give the carboxy radical **19**. Finally, decarboxylation produces the singlet excited ketone **21***, which generates light and ground-state ketone **21**. This scheme also offers, through the agency of **18** or **19**, an alternative pathway to by-pass **21***.

Our results further confirm the remarkably high thermal stability of 1,2,4-trioxan-5-ones. *E.g.*, the half-life of trioxanone **14** in 1-phenyldecane at 200° is 12.6 min and is *ca.* 1 h at 180°. Its activation energy is extremely high and comparable to that observed for *trans*-4,4-dimethyl-2,3,5-trioxabicyclo[4.4.0]decane (39.9 kcal/mol), a nonluminescent bicyclic 1,2,4-trioxane where the extrudable CO_2 moiety is lacking [21]. It is also worth noting that the activation energies of **13** and **14** are about the same as that of the exceptionally stable adamantylideneadamantane 1,2-dioxetane (35 ± 2.2 kcal/mol) [9].

The pre-exponential factor A of the *Arrhenius* relation for trioxanones **13** and **14** is *ca.* 10^{13}. This value is entirely compatible with unimolecular behavior. On the other hand, trioxanone **11** displays a smaller pre-exponential factor ($10^{7.3}$). Such a value is usually associated with more complex mechanisms [22]. It was shown elsewhere that the proton at C(6) in **11** can be abstracted by base [23]. Such an alternative avenue of reaction might be taken on thermolysis and could contribute to its faster rate of decomposition. The trioxanones **12**–**14**, which cannot undergo such deprotonation, all show similar values for the activation energy.

Conclusion. – The salient results of the present study are the confirmation of the thermal resilience of the 1,2,4-trioxan-5-one ring, the deduction that its fragmentation is not concerted, but occurs stepwise, and that light is indeed emitted, albeit inefficiently from singlet ketones uniquely derived from the C(6) end. Another important finding is the temperature dependence of the chemiluminescence quantum yields and its corollary, the greater value of E_{CL} over E_a, which points to the operation of dual pathways for decomposition.

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