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Thermal Stability of Spiro[adamantane-[1,2]dioxetanes]

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The thermal stability of several spiroadamantane-substituted 1,2-dioxetanes was determined by means of chemiluminescence (Table 1). The evident stabilization of dioxetanes by such substitution cannot be interpreted in terms of "inertial mass" or "torsional" arguments in the case of concerted decomposition nor by "compressional" arguments in the case of diradical decomposition. It is suggested that a *transoid* diradical **19t**, in which the engaged orbitals are antiperiplanar arranged, promotes C – C cleavage. The bulky adamantane substituent encumbers such conformational isomerization of the initially formed *cisoid* diradical **19c** into the preferred **19t**.

Thermische Stabilität von Spiro[adamantan-[1,2]dioxetanen]

Die thermische Stabilität einiger spiroadamantansubstituierter 1,2-Dioxetane wurde durch deren Chemilumineszenz bestimmt (Tab. 1). Die deutliche Stabilisierung des Dioxetans durch diesen Substituenten kann weder durch "inertial mass"- oder "torsional"-Argumente im konzertierten Zerfall, noch durch "compressional"-Argumente im radikalischen Zerfall interpretiert werden. Es wird vorgeschlagen, daß das *transoide* Diradikal **19t**, in dem die beteiligten Orbitale antiperiplanar angeordnet sind, die C – C-Spaltung begünstigt. Der sperrige Adamantanrest behindert die Konformationsänderung des zuerst gebildeten *cisoiden* Diradikals **19c** in das bevorzugte **19t**.

1,2-Dioxetanes are thermally labile substances which decompose usually at relatively low temperatures to afford electronically excited carbonyl products, manifested by their chemiluminescence (Eq. 1)[1]. For the isolated and characterized systems, their thermal stability can spread over a wide

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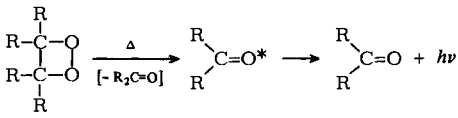


(1)

Table 1. Activation Parameters of 1,2-Dioxetanes[a)]

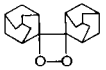
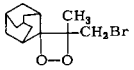
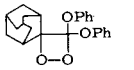
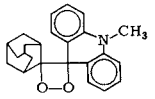
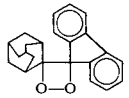
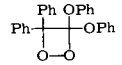
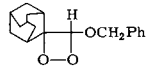
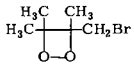
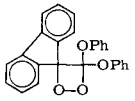
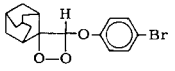
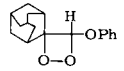
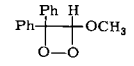
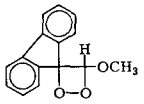
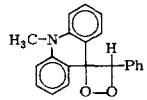
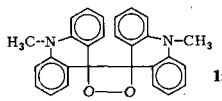
Dioxetane		$\Delta G^{\neq}$ at 293.2 K[b)] (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e. u.)	Ref.
	1	32.9	33.8 ± 1	+2.9 ± 2	2)
	2	29.4	28.4 ± 0.3	−3.5 ± 0.9	this work
	3	29.2	28.0 ± 0.2	−4.0 ± 0.6	this work
	4	28.0[c)]	(26.3)	(11.5)	9)
	5	26.9	25.8 ± 0.4	−3.7 ± 0.9	this work
	6	26.7	24.1 ± 0.4	−9.1 ± 1	this work
	7	26.4	25.0 ± 0.3	−4.7 ± 0.3	this work
	8	26.2	27.7 ± 0.1	+5.2 ± 0.4	10)
	9	25.8	25.0 ± 0.4	−2.8 ± 0.5	this work
	10	25.6	24.6 ± 0.3	−3.5 ± 0.3	this work
	11	25.2	23.4 ± 0.6	−6.0 ± 0.4	this work
	12	25.1[c)]	(26.1 ± 1)	(13.5 ± 0.6)	11)

Table 1 (*Continued*)

Dioxetane		$\Delta G^{\neq}$ at 293.2 K[b] (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Ref.
	**13**	22.8	20.8 ± 0.5	−7.0 ± 0.8	11)
	**14**	21.3[c]	(19.7)	(11.6)	9)
	**15**	18.6	18.2 ± 0.3	−1.4 ± 1.2	9)

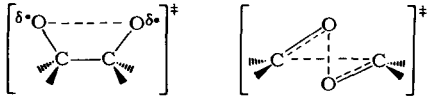
[a] Kinetic runs of this work were conducted in the temperature range of 350 – 400 K, the actual range depending on the particular dioxetane. At least four temperatures were chosen, covering a 15 – 20° temperature interval. Rate constants (k_{obs}) were run at least in triplicates, affording averaged values which were within 2 – 5% error limits. – [b] Estimated from the present *Eyring* activation parameters. – [c] Estimated from the published *Arrhenius* activation parameters which are given in parentheses.

temperature range, the bisspiroadamantane derivative **1**[2] figures as one of the most stable (Table 1), while the bisspiroacridan derivative **15**[3] represents one of the least stable (Table 1). Within the ca. 15 kcal/mol free energy difference between these two derivatives, one accommodates essentially all dioxetanes that are known to date. The unusually low thermal stability of the acridan system **15** is presumably due to intramolecular electron exchange decomposition[4], evidenced by the very high singlet excitation yield of this system[3]; but the unusually high thermal stability of the adamantane system **1** is still not well understood. Among the reasons that have been proposed to rationalize this remarkable stability of **1** have been:

(a) Initial oxygen-oxygen bond cleavage resulting in a dioxyl diradical, as shown in transition state **A**, is made difficult due to the rigidity and steric bulk of the adamantane rings leading to energetically unfavorable compression of these large groups and hence the greatly increased activation energy[2];

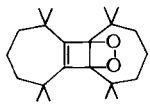
(b) A concerted torsional decomposition involving an unscrewing of the two adamantane units, as shown in transition state **B**, is resisted by the large inertial masses of the rigid adamantane units[4];

(c) Due to the planar four-membered ring in **1** and the hindered torsion about the carbon-carbon bond as the result of the bulky adamantane rings, a high activation energy is required for its concerted decomposition (transition state **A**)[5].



A **B**

An X-ray structure determination[4] clearly reveals that the dioxetane ring in **1** is not planar, but twisted out of plane by 21.3°. This deformation of the four-membered ring is in part due to the unfavorable nonbonded interaction of two pairs of equatorial hydrogens of the four methylene groups located under the dioxetane ring. It is these pairs of hydrogens that are responsible for the encumbered torsion around the carbon-carbon bond in the activated complex **B** of the concerted mechanism. Clearly, the argument (c)[5] that the planarity of the dioxetane ring is responsible for the remarkable stability of **1** does not apply since the dioxetane ring is significantly twisted. In fact, there appears not to exist a correlation between thermal stability and ring planarity for the few dioxetanes that have been X-rayed. For example, the cyclobuta-1,2-dioxetanes **16**[6] and **17**[7] have by necessity planar dioxetane rings; but while **16** is also one of the very stable dioxetanes[8] and **17** is quite unstable, both are significantly less stable towards thermolysis than **1**. The dioxetane ring in the planar **16** is structurally "locked in" and in the twisted **1** it is rotationally "locked in", so that their unusual thermal stability is completely different in origin.



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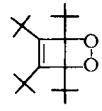

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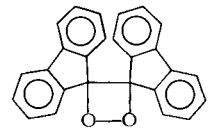


18

If the remarkable thermal stability of dioxetane **1** is due to the large inertial mass [argument (b)[4]] or the compression [argument (a)[2]] of the bulky and rigid spiroadamantane units, it appeared to us of interest to investigate the thermal stability of dioxetanes bearing one such spiroadamantane moiety. The inertial mass argument is still applicable, although at a reduced scale, while the compression argument can no longer uphold because two bulky units are essential. In fact, the stabilizing effect of a single spiroadamantane moiety is borne out in the dioxetane series **4**, **14** and **15**, cf. Table 1 for the necessary activation parameters. Thus, as already pointed out, dioxetane **15** is the least stable derivative that has been isolated[3]. Although **14** is somewhat more stable than **15**, introduction of one spiroadamantane moiety as in dioxetane **4** exerts a tremendous stabilizing effect[9]. Unfortunately, the rigid and bulky spiroacridan moiety in dioxetane **4** might in part be subject to compressional interactions with the spiroadamantane unit in the stepwise decomposition via transition state **A**. Furthermore, the inertial mass of the spiroacridan unit must be at least as large as that claimed[5] for spiroadamantane. We decided, therefore, to investigate a series of dioxetanes bearing one spiroadamantane moiety and determine their thermal activation parameters, in the hope of accounting for the stabilizing effect of this structural unit. Presently we report our results on this investigation.

Synthesis of 1,2-Dioxetanes

The preparation of the dioxetanes **1**[2], **4**, **14** and **15**[9], **8**[10], and **12** and **13**[11] are described in the cited references, while the new dioxetanes **2**, **3**, **5**, **7**, **10**, and **11** have been prepared in a previous paper[12]. Except for dioxetane **2**, which was prepared by the mercuration followed by bromination route[13], all the other derivatives were obtained either by photosensitized singlet oxygenation[14] of the olefin or the *Kopecky*[15] route. In the latter method the olefin is first converted into the β-bromohydroperoxide by treatment with 1,3-dibromo-5,5-dimethylhydantoin (DDH) and concentrated hydrogen peroxide (CAUTION!) and subsequently cyclized by dehydrobromination. The new dioxetanes **6** and **9**, which were required for comparison of their thermal

stabilities with those of the corresponding spiroadamantane derivatives, were prepared via the *Kopecky* route and the details are in the present Experimental Section.

Thermal Stabilities of 1,2-Dioxetanes

The activation parameters of all the new dioxetanes were determined by the isothermal kinetic method, monitoring the rate of dioxetane consumption by chemiluminescence as described in the Experimental Section. The data is summarized in Table 1. For ease of comparison the necessary activation parameter data of the known dioxetanes has been also included in Table 1. Although the activation enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) have been listed in Table 1 for information, for our discussion of stability trends we shall consider only the activation free energies ($\Delta G^{\neq}$). First of all, these data are usually more accurate and second of all, one avoids having to consider the problematic entropy factors.

The $\Delta G^{\neq}$ data in Table 1 bear out some interesting stability features about these 1,2-dioxetanes. Thus, the general conclusion emerges that the introduction of only one spiroadamantane moiety is sufficient to promote a significant stabilization of the dioxetane ring system against thermal decomposition. Restricting ourselves to our own data, this stabilization is worth ca. 1 – 4 kcal/mol in the $\Delta G^{\neq}$ values, i.e. up to ca. 1000-fold slower rates of decomposition. For example, replacement of the two methyl substituents in dioxetane **8** by the spiroadamantane moiety leads to **2**, which results in an increased thermal stability of ca. 3.2 kcal/mol in the $\Delta G^{\neq}$ values (Table 1). Similarly, replacement of the two phenyl substituents in dioxetane **6** by the spiroadamantane group leads to **3**, which is by ca. 2.5 kcal/mol more stable (Table 1). However, such replacement in dioxetane **12** leading to **7** brings only ca. 1.3 kcal/mol stabilization (Table 1), but we are not comparing strictly similar cases since **7** possesses a benzyloxy substituent and **12** a methoxy substituent. While we do not expect that this structural difference causes a dramatic effect on the stability of these dioxetanes, the influence could nevertheless be appreciable. For example, the *p*-bromophenoxy- and the phenoxy-substituted dioxetanes **10** and **11**, respectively, are by 0.8 and 1.2 kcal/mol less stable than the benzyloxy-substituted derivative **7**.

In all of the spiroadamantane-substituted dioxetanes that we have compared thus far, i.e. the derivatives **2**, **3**, and **7**, the second dioxetanyl carbon bears small and flexible substituents, e.g. bromomethyl, methyl, phenoxy, or benzyloxy. Consequently, destabilization of the transition state **A** in the diradical mechanism due to compressional effects [argument (a)[2]] is not applicable to rationalize the enhanced stability of these 1,2-dioxetanes. Also the suggestion that the enhanced stability exerted by the spiroadamantane units may derive from encumbered torsion about the carbon-carbon bond in the activated complex **B** of the concerted decomposition route [argument (c)[5]] is unreasonable because Dreiding models show that with only one spiroadamantane unit such restrictive motion is absent. We are, therefore, tempted to conclude that the stabilizing effect of the bulky and rigid spiroadamantane group in these dioxetanes is "inertial mass" derived [argument (a)[4]].

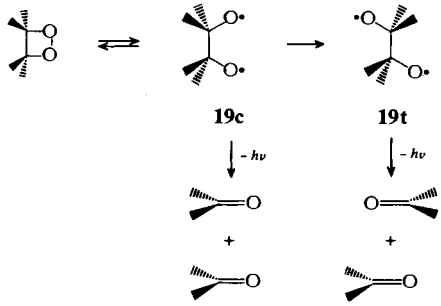
However, on this last point, a very informative set of dioxetanes is the series **3**, **5**, and **9**. First be it said that despite earlier claims[16], the bisspirofluorene-1,2-dioxetane **18** has

yet to be prepared. Presumably it is too unstable to survive isolation and characterization. Therefore, the fact that the spirofluorene-substituted dioxetanes **5** and **9** could be made and were sufficiently stable to allow purification and characterization indicates that the spiroadamantane group as well as the electron-withdrawing phenoxy groups stabilize thermally labile dioxetanes.

Replacement of the two phenoxy substituents or the spirofluorene group in dioxetane **9** by spiroadamantane groups to give **5** and **3**, respectively, results in more stable dioxetanes. The spiroadamantane stabilization is as expected greater for the **9** → **3** than for the **9** → **5** substitution, i.e. 3.4 versus 1.1 kcal/mol differences in the $\Delta G^{\neq}$ values (Table 1). This is due to the destabilizing effect of the spirofluorene moiety. Whatever the destabilizing influence of the spirofluorene group may be, it is definitely not of the electron exchange type as in the case of the spiroacridan group, since the spirofluorene moiety is not nearly as easily oxidized as the spiroacridan group. Furthermore, from the point of view of molecular bulk and rigidity, the spirofluorene group should be comparable to that of the spiroadamantane group. Consequently, on the basis of the "compressional" [2] argument in the diradical mechanism, i.e. transition state **A**, or the "inertical mass" [4] and the "torsional" [5] argument in the concerted mechanism, i.e. transition state **B**, the spirofluorene like the spiroadamantane moiety should stabilize 1,2-dioxetanes. Yet, quite the contrary obtains in that the spirofluorene group excerts a destabilizing effect on 1,2-dioxetanes. Most convincingly, while the bisspiroadamantane-1,2-dioxetane **1** is the most stable dioxetane that is known to date, the bisspirofluorene-1,2-dioxetane **18** is too unstable to be isolated. In fact, the spirofluorene moiety is more destabilizing than the spiroacridan group because the bisspiroacridan-1,2-dioxetane **15** could at least be isolated and characterized.

In view of these results we are obliged to conclude that the stabilizing influence of the spiroadamantane group in terms of "inertial mass" [4] on the concerted decomposition route [transition state **B**] is not very likely. Since for the dioxetanes **2**, **3**, and **7**, which contain only one spiroadamantane unit, the "compressional" effect [2] on the diradical mechanism [transition state **A**] or the "torsional" effect [5] (not requiring planarity of the dioxetane ring) on the concerted mechanism [transition state **B**] are inoperative, the stabilizing nature of the spiroadamantane moiety is still in want of a rational explanation.

One possible rationalization, but difficult to prove experimentally, is to propose diradical formation by oxygen-oxygen bond elongation, but the dioxyl diradical



(2)

fragments preferentially out of the *transoid* conformation (**19t**) rather than the *cisoid* conformation (**19c**), as shown in Eq. 2. On opening of the dioxetane ring the dioxetanyl carbons acquire the preferred sp^3 hybridization which accentuates the rotational barrier about the carbon-carbon bond due to increased nonbonded interaction of the substituents on the dioxetanyl carbons. For normally large substituents this is of no particular consequence and the rotational isomerization **19c** → **19t** is fast, so that the rate determining step is oxygen-oxygen bond fission. However, for bulky substituents such as spiroadamantane the rotational isomerization could be rate determining instead of peroxide bond cleavage[17]. This is to say, after breaking of the oxygen-oxygen bond, the *cisoid* diradical **19c** requires additional thermal activation to attain the preferred antiperiplanar arrangement of the interacting orbitals of the *transoid* diradical **19t**. Dreiding models suggest that such rotation would already be significantly encumbered even for one bulky spiro substituent in the 1,4-diradical **19**. In fact, such model inspection reveals that in the diradical derived from dioxetane **1** the pairs of methylene hydrogen of the spiroadamantane moieties prevent the rotational isomerization **19c** → **19t**. The unusual thermal stability of such bulky dioxetanes might possibly be of this origin.

Be this as it may, the most practical conclusion that we can deduce from our stability data (Table 1), is that the bulky and rigid spiroadamantane group is an effective tool for stabilizing otherwise thermally labile 1,2-dioxetanes. This synthetic concept has been effectively utilized in a previous paper[12], allowing us to prepare hitherto unknown 1,2-dioxetanes.

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Experimental Part

Synthesis of 1,2-Dioxetanes [General procedure for dioxetanes **6** and **9**]: A solution of 1.4 mmol ketene acetal[18] in 30 ml of ether was cooled to 0°C and 2.5 ml of 85% H_2O_2 carefully added while stirring magnetically. The ice bath was replaced by a dry ice-acetone bath (−75°C) and 203 mg (0.71 mmol) of 1,3-dibromo-5,5-dimethylhydantoin was added portionwise over a period of 10 min. After complete addition the mixture was allowed to warm slowly to 25°C (6 h). The pink reaction mixture was washed with water (2 × 25 ml), cold 10 % NaOH solution (2 × 20 ml) and water (25 ml). The ethereal bromohydroperoxide solution was diluted to ca. 80 ml with CH_2Cl_2 and then was added dropwise 4.0 g (large excess) NaOH in 30 ml water at 0°C while stirring mechanically. After stirring for 4 − 5 h at 0°C, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2 (2 × 25 ml). The extracts were combined with the organic layer and washed with water (2 × 25 ml), dried over anhydrous $MgSO_4$ and roto-evaporated (10°C/18 torr). The yellow residue was purified by silica gel chromatography at −40°C, using CH_2Cl_2 as eluant, and several recrystallizations from pentane/ether, affording the pure 1,2-dioxetanes in 17 − 22% yield.

3,3-Diphenoxy-4,4-diphenyl-1,2-dioxetane (**6**) was prepared via the above general procedure in 17% yield; m.p. 68 − 70°C (from pentane/ether). − IR (CCl_4): 3080, 3040, 1600, 1500, 1455,

1295, 1235, 1200, 1115, 1010, 1000, 940, 695 cm^{-1}. – ^{1}H-NMR (CCl_4): δ = 6.5 – 7.1 (m, 10H), 7.1 – 7.7 (m, 10H).

$C_{26}H_{20}O_4$ (396.5) Calc. C 78.77 H 5.09 Found C 78.51 H 5.41

4,4-Diphenoxyspiro[1,2-dioxetane-3,9'-fluorene] (**9**) was prepared by the above general procedure in 22% yield (yellow oil). – IR (CCl_4): 3080, 3050, 1600, 1500, 1455, 1300, 1270, 1225, 1210, 1195, 1185, 1160, 1070, 1040, 1005, 730, 690 cm^{-1}. – ^{1}H-NMR (CCl_4): δ = 6.4 – 7.0 (m, 10H), 7.0 – 7.5 (m, 8H), 7.85 – 8.1 (m, 2H). – ^{13}C-NMR ($CDCl_3$): Dioxetane carbons at δ = 98.79 and 118.55; aromatic carbon region shows extraneous peaks due to decomposition products.

Determination of Activation Parameters (General Procedure): A Packard scintillation vial, capped with a rubber septum, was charged with 3.0 ml of *o*-xylene[19] and the required volume of the 1,2-dioxetane solution in *o*-xylene was injected into the vial using a 10 µl Hamilton syringe. After efficient mixing by swirling at room temperature, the scintillation vial was transferred to the sample chamber of the Hastings-Mitchell photometer[20], which was maintained at a constant temperature by means of a Haake FJ thermoregulated bath. The emission decay was monitored continuously versus time over a 15 – 20° temperature range, using at least four temperature points. The activation parameters were calculated from the rate constant data by means of the *Eyring* equation[21], using a Hewlett-Packard 200 computer.

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$C_{26}H_{18}O_2$ (362.4) Calc. C 86.19 H 4.97 Found C 86.14 H 4.99

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