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Mendeleev Commun., 1991, **1(4)**, 124–125
Mendeleev Communications

Radiation Stimulated Cyclodimerization of Adamantan-2-one

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1,3- and 1,2-dioxetanes have been prepared by γ-radiolysis of adamantan-2-one solutions; the formation of the dioxetanes was assumed to follow the reaction of two radiation-excited ketone molecules.

The four-membered cyclic peroxides 1,2-dioxetanes undergo thermal decomposition to give excited, mainly triplet, carbonyl products.[1,2] Fig. 1 shows a representation of the energy levels

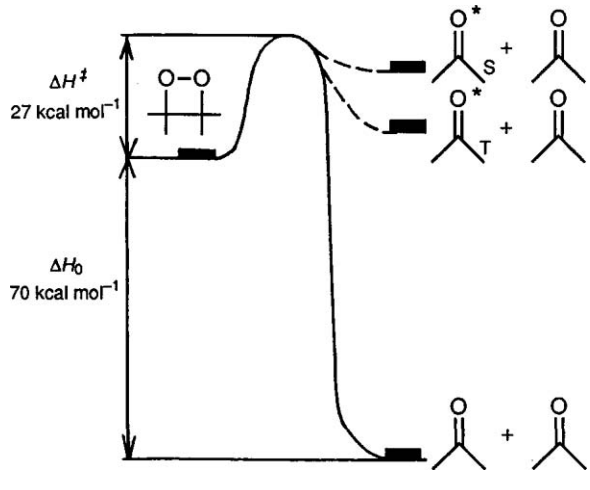


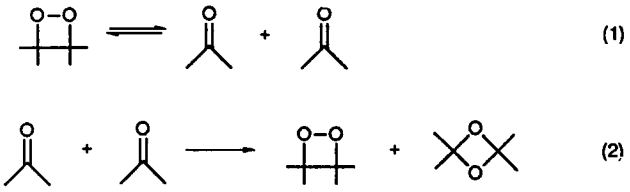
Fig. 1 The energetics of TMD decomposition

for the decomposition of 3,3,4,4-tetramethyl-1,2-dioxetane (TMD) into two molecules of acetone.[1]

The reaction, as described by the reversible eqn. (1), demonstrates a potential preparation of dioxetane *via* the retro-reaction of the decomposition, *i.e.* cyclodimerization of the ketone. It is also obvious that this pathway leads to both the 1,2- and 1,3-dioxaheterocycles [eqn. (2)]. However, it is necessary to overcome a rather high energy barrier (*ca.* 100 kcal mol^{-1} for TMD)† (see Fig. 1) for the cyclodimerization to afford 1,2-dioxetane.‡ Such an excess of energy can be exhibited only by two excited ketone molecules. For instance, a singlet-excited acetone molecule has an energy of only 84 kcal mol^{-1}, whereas the total energy of two triplet-state molecules of acetone is 156 kcal mol^{-1}.

Proceeding from the above consideration, we attempted the preparation of 1,2- or 1,3-dioxetanes *via* radiolysis of the ketone. It is well-known that excited-state molecules are generated by the effect of ionizing radiation on a substance. Photoexcitation is also successful. Indeed, 1,2- and 1,3-dioxetanes have been reported to be intermediates in the photolysis of acetone and acetaldehyde.[3,4] In this cases the dioxetanes were not isolated, although they were included in the reaction schemes, on the basis of indirect indications. We decided to investigate

† 1 cal = 4.184 J.



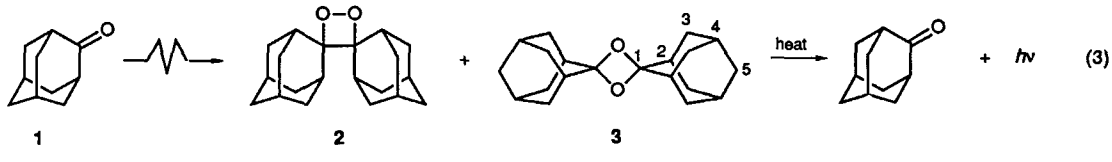
(1)

(2)

the radiolysis of adamantan-2-one **1**, because the skeleton substituents increase the stability of the dioxetanes.

A standard freeze–pump–thaw procedure was used to degas glass ampoules filled with 1.3 mol dm^{-3} solutions of **1** in MeCN, benzene or toluene. After that, the solutions were γ-irradiated (^{60}Co) at 25 °C with an exposure of 2.8×10^2 rad s^{-1}.§ The samples were then frozen in liquid nitrogen to prevent the decomposition of the radiolysis products. TLC analysis of the irradiated samples of **1** showed the appearance of two products.¶ A small amount of **2** was identified as 2,2′-epidioxy-2,2′-biadamantyl. The major radiolysis product **3** was believed to be the 1,3-dioxetane (2,2′; 2,2′-dioxydiadamantyl). This was confirmed by our studies of the thermolysis of **3** and by the spectral data.¶

The mass spectrum of **3** is similar to that reported[5] for **2**, except for a different ratio of intensity peaks displayed by the molecular ions and the major fragments. The IR spectrum of **3** shows a vibration frequency of the ether moiety. The proposed structure of **3** is confirmed by its NMR spectral assignments. Thermolysis of an irradiated solution containing **2** and **3** at 70–90 °C produces chemiluminescence (CL), which results in the regeneration of **1**. The above data suggest that reaction (3) occurs.



(3)

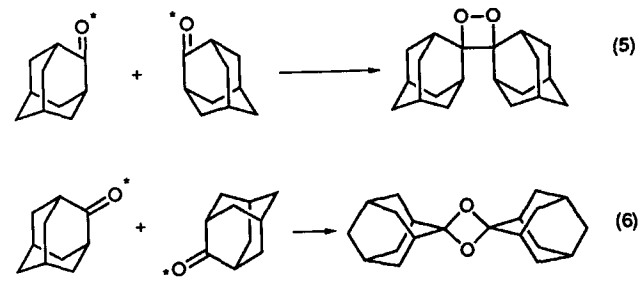
1 **2** **3**

The non-activated CL is due to a known process,[5] whereby $\mathbf{1}^{\ddagger}$ is generated upon the thermolysis of **2**. The CL is characterized by specific spectral parameters and activation energy values. In the presence of 9,10-dibromoanthracene (DBA) as a triplet energy acceptor, the CL intensity curve becomes rather intricate, although the generation of $\mathbf{1}^{\ddagger}$, from the slowly decomposition of **2** at the temperatures used, produces a constant intensity of DBA luminescence within a particular period of measurement. Hence, the CL activated by DBA is connected not only with the decomposition of **2** but also with the formation of triplet products, most likely $\mathbf{1}^{\ddagger}$ resulting from the decomposition of **3**, the latter being less stable than **2**. This was ascertained by studies of the CL exhibited by isolated **3**. In the absence of DBA, no CL is observed, *i.e.* $\mathbf{1}^{\ddagger}$ is not formed upon the thermolysis of **3**. The intensity of the activated CL decreases with lower concentrations of **3**. As follows from a comparison of the light intensities, the yield of $\mathbf{1}^{\ddagger}$ is much lower upon the decomposition of **3** than it is from decomposed **2**. The ratio of triplet yields upon the decomposition of **2** and **3**, was estimated as 10^3. Nevertheless, the formation of triplet products is a common feature of the decomposition of both 1,2- and 1,3-dioxetanes. Therefore, the decomposition of **3** can be described by eqn. (4).

$$\mathbf{3} \rightarrow \mathbf{1} + \mathbf{1}^{\ddagger} \qquad (4)$$

Upon thermolysis, the CL intensity curves become straighter, showing the characteristics of a first-order reaction. The activation parameters for the decomposition [$E_a = 26(\pm 2)$ kcal mol^{-1}, $\lg A = 12.5(\pm 1.0)$ s^{-1}] were obtained from the temperature dependence of the corresponding rate constants. Thus, the thermal stability of **3** is much lower than that of **2** ($E_a = 34$ kcal mol^{-1}).[5]

In order to estimate the radiation chemical yields of the radiolysis products, the amount of **2** was found by the CL method, *i.e.* by the intensity values under otherwise equivalent conditions; the amount of **3** was determined by weighing after column chromatography. After radiolysis of benzene solutions of **1**, $G(\mathbf{2}) = 0.08(\pm 0.02)$, $G(\mathbf{3}) = 4.0(\pm 0.3)$ molecules/100 eV with an irradiation exposure of 5×10^6–4×10^7 rad.



(5)

(6)

It is evident that several factors are responsible for the higher yields of **3** *versus* **2**. There is no doubt that the bulky adamantyl groups interfere with the cyclodimerization of **1** to **2**, and the latter is probably formed due to the rather bent structure of the excited carbonyl group [eqn. (5)]

The steric hindrance of the formation of 1,3-dioxetane is much weaker [eqn. (6)]. Compound **3** may also be assumed to result from the simpler reaction $\mathbf{1}^{*} + \mathbf{1} \rightarrow \mathbf{3}$, which requires less energy. One should also take into consideration the fact that the recombination of the radical products $\mathbf{1}^{+}$ and $\mathbf{1}^{-}$ may also contribute to the formation of **2** and **3** upon radiolysis. The 1,3-heterocycle is believed to be formed by the latter reaction.

We thank Dr L. M. Khalilov for his kind assistance in interpreting the ^{13}C NMR spectrum of **3**.

Received in USSR, 23rd April 1991
Received in UK, 1st August 1991; Com. 1/02109E

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‡ The energy barrier for cyclodimerization of two carbonyl groups to give 1,3-dioxetane should be lower than that for the reaction resulting in 1,2-dioxetane. It has recently been reported that a simple thermal reaction leads to cyclodimerization of 5-norbornen-2-carboxaldehyde to 1,3-dioxetane (D. Bankston, *J. Org. Chem.*, 1989, **54**, 2003). We believe that this is improbable.

§ 1 rad = 0.01 Gy.

¶ TLC: Silufol, hexane–$CHCl_3$ (3:2). R_f (**2**) = 0.42, R_f (**3**) = 0.2. *Spectral assignments* for **3**: MS (*m/z*) 300(0.3%), 284(0.7), 268(100), 150(70); IR ν/cm^{-1} 1072 (COC); ^{13}C NMR ($CDCl_3$) δ 127.79(C^{-1}), 38.77(C^{-2}), 37.29(C^{-3}, 27.91(C^{-4}), 35.84(C^{-5}).