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INVESTIGATIONS ON THE THERMAL DECOMPOSITION OF 1,2-DIOXETANES VIA DSC

Some peculiarities concerning the sample preparation

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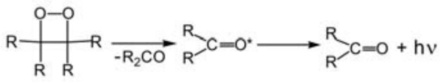
Abstract

Reproducible measurements, reliable results and 1st order kinetics for the whole reaction are obtained during the thermal decomposition of dioxetanes only, if inclusions of impurities in commercial sample pans are blocked by additional thick (magnitude of 100 μm) and close Al_2O_3 protective layers. As a rule, nearly the same activation parameters are then found both for the decomposition of solvent-free dioxetanes and diluted solutions in several solvents. Mixtures of different dioxetanes in the same solvent contribute independently to the overall heat flow rate.

Keywords: dioxetane, kinetics, sample pan pretreatment, thermal decomposition

Introduction

1,2-Dioxetanes are high-energy and thermally labile substances with a four-membered cyclic system with two adjacent oxygen atoms. They decompose at relatively low temperatures into carbonyl fragments [1], apparently by simple symmetric cleavage of the oxygen-oxygen and the carbon-carbon bond. A relatively large amount of the reaction energy, typically 10 to 30%, is lost as light. Our interest in this reaction stems not only from the experimental observation of 'cold light' but also from the theoretical problem of understanding the mechanism of dioxetane decomposition [2]. A very simplified reaction mechanism is:



The four substituents *R* may be equal or different. One of the two carbonyl fragments is formed in the normal electronic ground state. The considerable reaction en-

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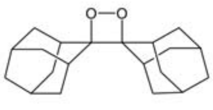
ergy (between –300 and –400 kJ mol^{-1}) is sufficient to excite electronically the second fragment, but the amazingly high ratio of triplets to singlets (100–1000) is unusual and should be explained by details of the reaction mechanism. Traditionally, since the early seventies of the last century three mechanisms have been postulated for the thermal decomposition of dioxetanes, for a detailed discussion [3–6]. Briefly said, the one extreme is the synchronous, concerted mechanism. O–O and C–C bond are weakened equally at the transition state. In the other extreme a stepwise, biradical mechanism is postulated. At first the weaker O–O bond breaks completely resulting in an oxygen-oxygen biradical. There are a large number of experiments with substituted dioxetanes whose results can be explained better by the one or other extreme. Newer works from Murphy and Adam [5] strongly support the asynchronous concerted [7] or merged mechanism. The O–O bond is initially more weakened than the C–C bond. Nevertheless, this results in an at least partial radical character of the intermediate and seems to be important for the interpretation of some of our experimental findings.

To our knowledge, the activation parameters of thermal decomposition of 1,2-dioxetanes were nearly exclusively determined by isothermal methods [8] using chemiluminescence measurements in inert solvents. As a rule, the investigated temperature range is relatively small, frequently not larger than 15–20 K and the absolute temperature rarely exceeds 80°C. A simple 1st order kinetics is found for the overall reaction in the predominant number of investigations. Surprisingly, up to now only one older experiment [9] was published using the differential scanning calorimetry (DSC). If the decomposition is investigated in closed sample pans, the total part of the emitted radiation is completely converted into heat and the instantaneous heat flow rate is a measure for the rate of the dioxetane decomposition. The investigation of the reaction with a number of different heating rates supplies more reliable kinetic results than isothermal scans in a relatively narrow temperature window. This is valid for arbitrary other reaction types, for the traditional investigations of curing reactions as well as for the reliable determinations of TTT cure diagrams [10] or the decomposition of new high-energetic materials [11].

Experimental

We have used the 1,2-dioxetanes I–VI. They were prepared by photooxygenation of the corresponding olefines at –20°C in methylenechloride [12–14]. The dioxetanes 1–4 ($\underline{1}$: crystalline, T_{fus}: 164°C [9]; $\underline{2}$: crystalline, T_{fus}: 109°C; $\underline{3}$ and $\underline{4}$: amorphous) can be stored several years at 5°C, $\underline{5}$ and $\underline{6}$ ($\underline{5}$: crystalline, T_{fus}: 34.5°C; $\underline{6}$: amorphous) decompose slowly already at ambient temperature.

The DSC measurements are carried out with the DSC 7 (PerkinElmer). As usual, the instrument was checked in the temperature range of –20 to 230°C concerning base line, temperature (water, indium and tin), heat (indium) and heat flow rate (sapphire). Only the nonisothermal reaction mode was appropriated for these measurements. The heating rates were varied between 0.25 and 16 K min^{-1}. In all cases the changes of the total heat capacity of the reaction mixture during the reaction were negligible. Therefore,



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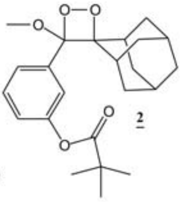

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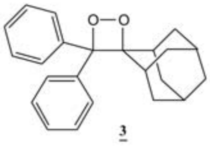

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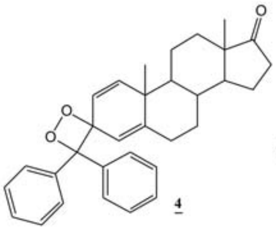

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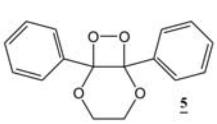

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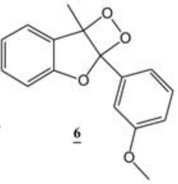

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the zeroline curvature, overlaying the raw signal of the DSC-7 measurement, was removed reliably by subtracting a second run with the mixture completely reacted.

The decomposition reaction was investigated in sealed aluminium sample pans for volatile substances, both with the pure dioxetanes and in differently concentrated solutions of *o*-dichlorobenzene, xylene or 1-acetylnaphthalene. The first two solvents were purified by distillation. 1-acetylnaphthalene (boiling point 301°C) must be used if the reaction goes to completion at temperatures higher than 200°C. A certain disadvantage is then the clearly smaller solubility of the dioxetanes in this solvent.

Results

The most striking feature of our first measurements was their irreproducibility, strongly dependent on the dioxetane (extremely at 1, pronounced at 2, 4 and 5) and the sample preparation. With exception of 2 and 3, measurements with pure dioxetanes couldn't evaluated at all, as a rule their peaks were differently structured in addition. Scattering results were also obtained with concentrated solutions, only measurements with strongly diluted solutions (less than 1 mg dioxetane in 10 mg of solvent) were relatively reproducible and showed the expected simple first order kinetics.

Additional characteristic deviations from a simple 1st order kinetics were observed in solutions of 1 and 2, again within a larger scatter range in spite of apparently the same conditions. Typical runs – that means, we concentrate on the mostly obtained curves within the scatter range – are shown in the Figs 1 and 2 for solutions of 2 in *o*-dichlorobenzene. In every case the decomposition started as 1st order reaction. The higher the mass fraction of the dioxetane the more pronounced was an additional effect (Fig. 1). But somewhat surprisingly we have found the same also for increasing sample masses at a given mass fraction (Fig. 2). A possible autocatalysis cannot be responsible for this observation because the dependence of the reaction rate from the sample size or the mass fraction of the dioxetane is a distinct signpost against it. Nevertheless, we have experimentally excluded autocatalysis, addition of the reaction product was without any influence.

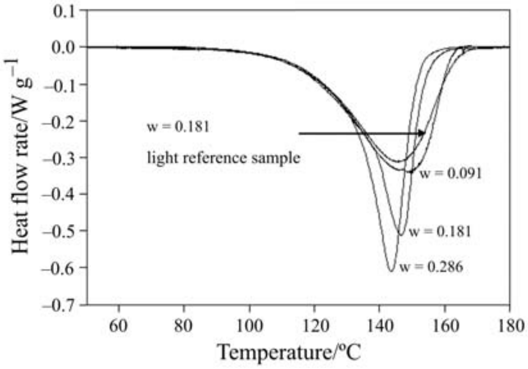

Fig. 1 The dependence of the reaction behaviour on the mass fraction of the dioxetane 2 in *o*-dichlorobenzene, large sample masses (≅ 20 mg), $\beta = 4$ K min^{-1}. The light sample with $m = 6.62$ mg is used as reference showing simple 1st order kinetics

Two possibilities could be responsible for this behaviour. The first one assumes the existence of radical intermediates according to an assumed biradical mechanism [3–6]. It is well known that chain termination reactions are caused by three-body collisions and by collisions at the wall. The solutions tend to spread over the inner surface of the sample pans. That way, the probability for chain termination reactions due to collisions at the wall is inversely proportional to the sample mass (volume).

A second and surely nearby suspicion is that any inhibitor is present and that the reaction rate dramatically increases after its complete consumption. Lechtken [15] has suggested that triplet states, produced during the thermal decomposition of dioxetanes, are deactivated by the oxygen of aerated solutions faster than they sensitise the destruction of another molecule of the dioxetanes. In other words, if oxygen is absent or consumed a considerable part of the decomposition of the dioxetanes should occur as the direct result of interaction with this electronically excited cleavage product. The reaction rate increases considerably despite decreasing amount of

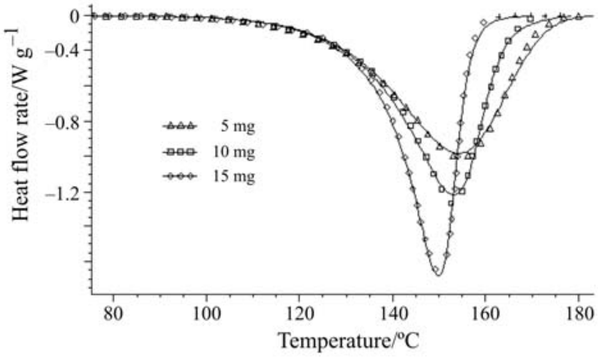

Fig. 2 Influence of the total sample mass on the kinetics of thermal decomposition of 2 in mesitylene. $\beta = 8$ K min^{-1}; $w = 0.22$; symbols: experiment, solid lines: model calculation

the dioxetane. Small samples and very diluted solutions contain sufficient solved and gaseous oxygen. If larger mass fractions of the dioxetanes and/or higher sample volumes are used, the total amount of oxygen is no longer sufficient to deactivate the intermediate and deviations from the first order kinetics are observed. If this additional 'induced' decomposition of the dioxetane is assumed, the fit of the experimental 'typical' curves shown in the Figs 1 and 2 is possible in principle [16].

Both possibilities cannot explain the generally observed marked scattering range of the measurements using apparently same experimental conditions. Many unsuccessful experiments were made before we have found the reason for it. The actual cause is the influence of trace impurities in the aluminium sample pans! Usual solvent cleaning of the sample pans (including ultrasonic cleaning) was ineffective. The electron micrograph of a PerkinElmer sample pan for volatile substances (Fig. 3) shows in the aluminium base material a number of inclusions of about 1–2 μm diameter. The scanning electron microscopy with energy dispersive X-ray analysis has clearly shown that besides Fe and Si also Cu and Ag are enriched in the inclusions, the corresponding EDX-spectrum is shown in Fig. 4. Already for a long time [17, 18] it is well-known that trace amounts of impurities (above all transition metal ions as Cu^{2+} and Ni^{2+}) strongly catalyze the decomposition of some dioxetane solutions. The suggested solution to prevent such influences consists in the pretreatment of the used solvents with ethylenediaminetetraacetic acid (EDTA). Of course, this cannot be effective in our case and also the pretreatment of the sample pans in EDTA-solution was ineffective.

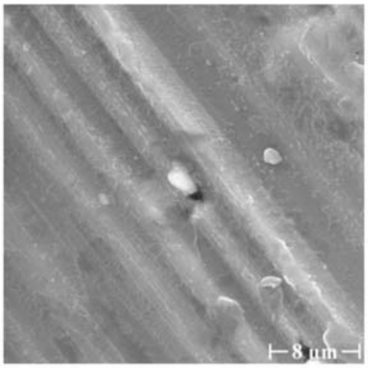

Fig. 3 Electron micrograph of the surface of an untreated PerkinElmer sample pan for volatile samples. Inclusions of 1–2 μm diameter are clearly recognizable in the aluminium base material

The natural Al_2O_3-protective layer (5–10 μm) of the sample pans is obviously too thin to isolate the dioxetane from the cupreous inclusions. Therefore, we have used the following procedure for a distinct thickening of the protective layer:

- treatment with 2M NaOH for 3 min at room temperature
- treatment with 0.05M H_2SO_4 for 3 min at room temperature
- boiling with distilled water for 1 h

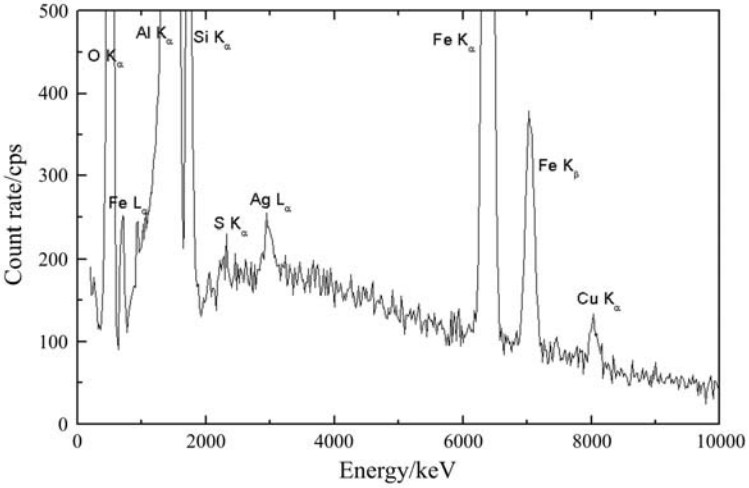

Fig. 4 EDX-spectrum (scanning electron microscopy with energy dispersive X-ray analysis) of the inclusions in the base material. The inclusions are enriched with Cu and Ag, additional Si and Fe impurities are most probably irrelevant for our investigations

After this procedure, the ellipsometry proves that the thickness of the Al_2O_3-protective layer is increased by 100–120 μm. The success of this pretreatment is impressive! Measurements in pans with a thick protective layer are absolutely reproducible. This is true even for solvent-free pure dioxetanes. The distinct influences of sample mass and/or mass fraction of the dioxetane (Figs 1 and 2) are completely absent. The Figs 5 and 6 show measurements of the same dioxetane 2 in a very concentrated solution of

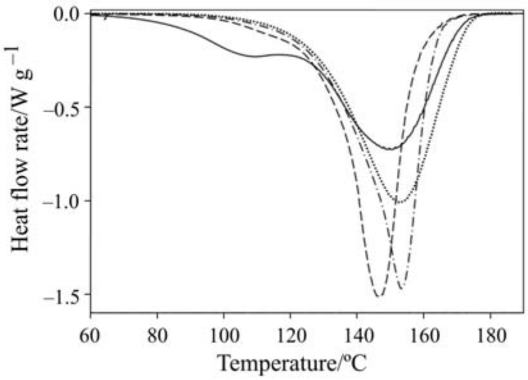

Fig. 5 Extremely scattering decomposition curves of dioxetane 2 in *o*-dichlorobenzene in untreated PerkinElmer sample pans for volatile samples. Mass fraction: 0.275; $\beta = 8$ K min^{-1}; solid line: 14.98 mg, dashed line: 10.21 mg and dash-dotted line: 18.89 mg; the dotted line serves as reference for a regular first order kinetics as obtained in pretreated sample pans (*m*: 19.08 mg)

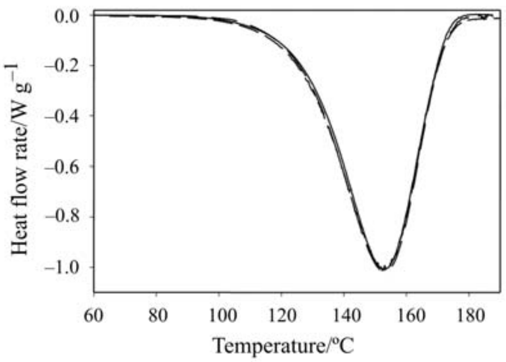

Fig. 6 Reproducible decomposition behaviour in pretreated sample pans with a 100 μm protective layer of Al_2O_3. Exactly the same substances and heating rates as in Fig. 5; solid line: 10.33 mg, dashed line: 15.03 mg and dash-dotted line: 19.08 mg

o-dichlorobenzene (mass fraction: 0.275) in untreated (Fig. 5) and pretreated (Fig. 6) sample pans. Of course, not all measurements in untreated sample pans differ so strongly, but the curves of Fig. 5 provide a good impression of the variation range.

From this we can conclude that deviations from a simple 1st order kinetics are triggered by traces of catalytic impurities, probably Cu in our case. This is true whether one favours radical intermediates or electronically excited cleavage products to interpret the observed behaviour. The bad reproducibility of measurements in untreated sample pans despite apparently same experimental conditions is now also understandable. Number and size of the inclusions in the base material are subject to large fluctuations for the individual sample pans.

However the true mechanism may be in presence of catalytic impurities, we have now a reliable procedure in order to avoid such complications. The obtained reaction energies and activation parameters are summarized in Table 1, which shows also the results for the decomposition of the pure solvent-free dioxetanes investigated by us ($\underline{1}$, $\underline{3}$ – $\underline{5}$). With exception of $\underline{1}$, the differences of the activation parameters for dilute or highly concentrated solutions and for pure solvent-free substances are very small. This is equivalent to the conclusion that the used solvents don't have a significant kinetic solvent effect. It must be mentioned that the non-linear optimization procedure for a chosen kinetic model [19, 20] always supplies the best global solution for the used data set. But the actually obtained best solution for lg$A$ and E_A of the 1st order reaction is somewhat influenced by unavoidable and randomly distributed experimental errors. That means, very small differences in the decomposition rates between solutions and solvent-free substances are described by statistical scattering combinations for lg$A$ and E_A. In such cases it is helpful to keep constant one of the two activation parameters. If we use constant values for E_A, the slightly higher values for lg$A$ reflect the slightly higher decomposition rate of solvent-free substances. Figure 7 shows the DSC curves for the decomposition of the dioxetanes $\underline{2}$ and $\underline{3}$ in substance (solid lines) and in *o*-dichlorobenzene (broken lines). The heating rate was 8 K min^{-1}, an analogous result is found at other heating rates. The preceding endothermic peak of 2 (solid line) corresponds to the melting of the solid. Without going into the details, a modelling of the complete curve is successful according to a mechanism with two consecutive reactions.

Table 1 Activation parameters and reaction energies for the 1st order decomposition of the investigated dioxetanes, nearly independent on the mass fraction for the dioxetanes 2–6 in *o*-dichlorobenzene, xylene or 1-acetylnaphthalene

Dioxetane	$\lg A/\mathrm{s}^{-1}$	E_A /kJ mol^{-1}	Q /kJ mol^{-1}	Comment
1	12.64±0.04	134.3±1.0	–276.1±3.2	$w = 0.029$
	11.65±0.06	124.1±1.5	–279.2±5.1	$w = 0.165$
2	13.53±0.01	126.4±0.8	–323.3±3.4	
	13.61±0.02	126.5±1.0	–310.1±4.0*	solvent-free
3	13.49±0.02	116.7±0.4	–162.6±4.9	
	13.55±0.02	116.7±0.5	–155.9±2.7	solvent-free
4	12.41±0.01	105.9±1.2	–231.6±2.7	
	12.58±0.01	105.9±1.5	–225.1±4.2	solvent-free
5	11.21±0.02	94.9±0.3	–324.5±10	
6	11.45±0.01	91.6±0.2	–252.9±9.2	

** uncertain reaction energy due to partial overlapping of melting and reaction peak (Fig. 7)*

Contrary to the dioxetanes 2–5, the decomposition of 1 can be investigated only in solutions with $c < 1$ mol L^{-1}. Furthermore, we observe now a distinct dependence of the activation parameters on the mass fraction (Table 1). The decrease of the $\lg A$ with increasing mass fractions is more than compensated by decreasing E_A's. Such a result – but to a much smaller extent – would be probably obtained also for the dioxetanes 3–5, if 'error-free' measurements were available.

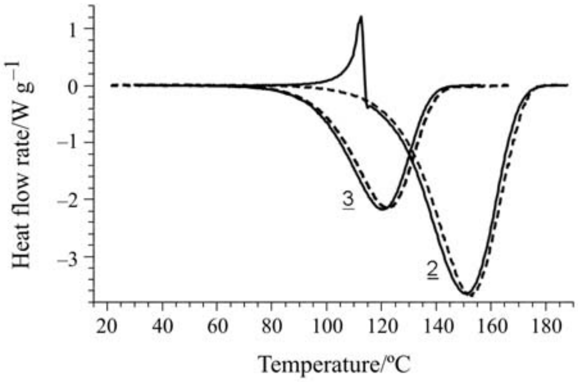

Fig. 7 Comparison of the decomposition curves of the two dioxetanes 2 and 3 with and without solvent; solid lines: solvent-free substances, broken lines: in *o*-dichlorobenzene (mass fraction 0.275 for 2 and 0.205 for 3); $\beta = 8$ K min^{-1}

The decomposition kinetics of the dissolved dioxetanes is not changed in mixtures with another dioxetane. We have investigated several mixtures of 1 and 3 in 1-acetylnaphthalene. In any case, the measured DSC curves can be perfectly modelled by two parallel reactions using the activation parameters of the pure dioxetanes.

Conclusions

The DSC technique is a fast and suitable method for the investigation of the thermal decomposition of 1,2-dioxetanes, although the first measurements resulted in apparently contrary results.

Commercial Al sample pans (at least with the Al used by PerkinElmer) contain traces of other elements, Fe, Si, Cu and Ag. At least for Cu or Cu^{2+} it is known [17, 18], that very small traces catalyze the decomposition of the dioxetanes.

The natural Al_2O_3-protective layer of the sample pans is obviously too thin to protect the dioxetane from these inclusions. We suggest a simple procedure to obtain much thicker protective layers (magnitude of 100 μm). Measurements in these pretreated sample pans are absolutely reproducible and form a reliable base for kinetic evaluations.

With exception of the dioxetane 1, nearly the same activation parameters are found both for the decomposition of solvent-free dioxetanes and diluted solutions in the used solvents.

Any interactions of different dioxetanes in the same solvent were not observed, they contribute independently to the overall heat flow rate.

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