3,3-Dimethyl-4[2-methyl-1-propenyl]-1,2-dioxetane:
Its Thermal Stability and Chemiluminescent Properties

Waldemar Adam* and Omar Cueto

Institut für Organische Chemie der Universität Würzburg, D-8700 Würzburg, Am Hubland, BRD and
Departamento de Química, Universidad de Puerto Rico, Rio Piedras, Puerto Rico 00931, USA

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1,2-Dioxetanes, Chemiluminescence, Activation Parameters, Excitation Yields, Solvent Effects

The alkenyl-substituted 1,2-dioxetane (1) was prepared by photosensitized singlet oxygenation of 2,5-dimethyl-2,4-hexadiene and its activation and excitation parameters determined. It is shown that dioxetane (1) is comparable in its thermal stability to alkyl-substituted dioxetanes and an inefficient chemical source of electronic excitation.

The photosensitized singlet oxygenation of 2,5-dimethyl-2,4-hexadiene was reported [1] to give the 3,3-dimethyl[42-methyl-1-propenyl]-1,2-dioxetane (1). Although this 1,2-dioxetane could be isolated and purified by low temperature (0 °C/0.1 Torr) distillation and characterized spectroscopically [1], its thermal and chemiluminescent properties were not reported. Since 1 represents one of the few reported 1,2-dioxetanes which bear alkenyl substituents [2], it was of interest to assess its thermal stability and compare it with other trialkyl-substituted derivatives, e.g. trimethyl-1,2-dioxetane.

More importantly, since on thermolysis dioxetane (1) would afford electronically excited α,β-unsaturated carboxylic (2) (eq. 1), it should be of interest to determine its efficiency of chemi-excitation and spin state selectivity, i.e. its singlet (\( \Phi^s \)) versus triplet (\( \Phi^t \)) excitation yields.

\[
\begin{align*}
\text{1} & \rightarrow \text{2} + \text{H}^* \\
& \text{(eq. 1)}
\end{align*}
\]

The pure (98 ± 1%) by iodometry) dioxetane (1) was obtained as yellow oil (after distillation at 0 °C/0.1 Torr) in the photosensitized singlet oxygenation of a 0.1 M solution of 2,5-dimethyl-2,4-hexadiene in methanol, using Rose Bengal as sensitizer and a 150-W high pressure sodium lamp as irradiation source. The direct chemiluminescence that was observed on heating of 1 served as monitor of the kinetics. Using a 4.57 \times 10^{-3} M solution of 1 in xylene (mixture) in the temperature range 325 to 345 K, good first order kinetics out to more than four half-lives could be realized. An Eyring analysis, i.e. ln (k/T) versus 1/T, of the rate data gave the activation parameters \( \Delta H^* = 21.6 \pm 0.6 \) kcal/mol, \( \Delta S^* = -7.6 \pm 1.0 \) e.u. and \( \Delta G^* (293.2 \mathrm{~K}) = 23.8 \pm 0.8 \) kcal/mol. This corresponds to a half-life of 20 h at 20 °C. Comparison with trimethyl-1,2-dioxetane [3], for which the half-life is ca. 55 h at 20 °C [3], confirms that alkenyl substituents in 1,2-dioxetanes does not affect their thermal stability considerably. This matches earlier conclusions that normally substituents, e.g. alkyl, aryl, alkoxy, etc. do not influence greatly the thermal stability of dioxetanes, an experimental fact which has led to the postulation of the diradical mechanism [4].

The direct chemiluminescence of dioxetane (1) is sufficiently intense to permit measurement of its chemiluminescence spectrum. Decomposition of 1 as 1.0 M solution in xylene (mixture) at 50 °C directly in a Perkin-Elmer MFP3B spectrophotometer gave a broad, unstructured emission extending from 350–500 nm with a maximum at 420 nm. This emission matched well the fluorescence spectra of 3-methyl-2-butenal (2), of acetone, or of a mixture of the two. Neither in methanol nor in methanol-trifluoroacetic acid mixtures was it possible to resolve the emissions of the two carbonyl products, so that we could not ascertain which of the two or whether both become chemi-excited during the thermolysis of 1. In fact, also the direct chemiluminescence quantum yields (\( \Phi^\text{DC} \)) remained relatively constant, i.e. \( \Phi^\text{DC}=3 \) to \( 10 \times 10^{-2} \) Einstein/mol, in these various solvents.

Since it is not known which of the two carbonyl fragments is chemi-excited during the thermolysis, it was necessary to determine its efficiency of chemi-excitation and spin state selectivity, i.e. its singlet (\( \Phi^s \)) versus triplet (\( \Phi^t \)) excitation yields.

\[
\begin{align*}
\text{1} & \rightarrow \text{2} + \text{H}^* \\
& \text{(eq. 1)}
\end{align*}
\]
of 1, and if both are energized, in what relative amounts, it is not possible to calculate the singlet excitation yield ($\Phi^S$) from the above direct chemiluminescence yield ($\Phi^{DC}$). Consequently, we turned to energy transfer chemiluminescence [5] to determine the excitation parameters, i.e., 9,10-diphenylanthracene (DPA) for singlet yields ($\Phi^S$) and 9,10-dibromoanthracene (DBA) for triplet yields. The results are summarized in Table I.

Table I. Excitation parameters$^a$ for 1,2-dioxetane (1)$^b$
b by DPA-energy transfer chemiluminescence$^c$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi^S$ (%)$^d$</th>
<th>$\Phi^T$ (%)$^e$</th>
<th>$\Phi^{T+S}$ (%)</th>
<th>$\Phi^T/\Phi^S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>0.0039</td>
<td>0.28</td>
<td>0.28</td>
<td>70</td>
</tr>
<tr>
<td>Methanol-Xylene</td>
<td>0.0043</td>
<td>0.23</td>
<td>0.23</td>
<td>50</td>
</tr>
</tbody>
</table>

$^a$ Values are reproducible within an error of ca. 20%;
$^b$ [(1)] = 4.57 $\times$ 10$^{-3}$ M;
$^c$ Method is described in ref. [5];
$^d$ DPA energy transfer;
$^e$ DBA energy transfer.

These excitation data (Table I) show that the total yield of excited states ($\Phi^{T+S}$) is quite low. Within the experimental error (ca. 20%) the total excitation yield is independent of solvent polarity. The possibility that the low total excitation yield might have arisen from competitive Paterno-Büchi reaction (oxetane formation) between acetone and butenal (2) was excluded by means of control experiment with the authentic substances. However, energy dissipation via cis-trans isomerization or oxetene formation [6] are still viable reasons for the low total excitation yields. Such intramolecular processes could compete efficiently with energy transfer to DPA and DBA, thereby leading to low $\Phi^{T+S}$ values. Experiments are in progress to explore these possibilities.

Like for most dioxetanes that yield $n,\pi^*$ excited states [2], the spin state selectivity ($\Phi^T/\Phi^S$) of (1) is quite high. Again, within experimental error the $\Phi^T/\Phi^S$ values are independent of solvent.

It is our contention that it should be of interest to study in detail a series of alkenyl-substituted 1,2-dioxetanes such as 1 in order to rationalize their low excitation yields. For this purpose more convenient synthetic methods are being developed to make such dioxetanes readily accessible.

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b) G. B. Schuster, Acc. Chem. Res. 12, 366 (1979);