Photocycloaddition of 2-aminoacrylonitriles to substituted 1-acetonaphthones: Determination of the quenching rate constants

H R Memarian* & M Nasr-Esfahani
Department of Chemistry, Faculty of Sciences, University of Esfahan, Esfahan 81744 Iran
H Görner
Max-Plank-Institut für Strahlenchemie, D-45470 Mülheim/Ruhr, Germany
and
D Döpp
FB 6/Organische Chemie, Gerhard-Mercator-Universität-GH-Duisburg, D-47048 Duisburg, Germany
Received 21 July 2000; accepted (revised) 12 June 2001

The triplet excited state of substituted 1-acetonaphthones 1b-i, as monitored by triplet-triplet (T-T) absorption spectroscopy, is quenched by two captodative olefins, 2-morpholinoacrylonitrile 2a and 2-piperidinoacrylonitrile 2c with rate constants approximately two orders of magnitude below the diffusion controlled limit. Formation of any intermediates, such as exciplex or diradicals resulting from interaction of the excited triplets with 2a,c could not be observed within the accessible wavelength range of monitoring (380-700 nm).

Photoadditions of 2-morpholinoacrylonitrile 2a and 2-(t-butylthio)acrylonitrile 2b to electronically excited acylnaphthalenes (1- and 2-naphthaldehye, 1-acetonaphthone 1a and 1-naphthophenone) have been reported earlier1. The major and truly efficient route of these reactions is [4+2]-addition of 2a,b to the 1,4-positions of the naphthalene. Only in the case of 1a has 1,2-addition of 2a been reported1, but evidence is accumulating 2 that fast [2+2]-addition to the 1,2-position precedes the 1,4-additions and that 1,4-adducts are formed at the expense of the (more light sensitive) 1,2-adducts as the starting acylnaphthalenes (acting as light screens) are consumed. The [4+2]-1,4-additions are of remarkably high regio-, stereo- and diastereoselectivity 1,3,4. In a more recent study, we observed the [2+2]- and [4+2]-photoaddition of 2-morpholinoacrylonitrile 2a5 and 2-piperidinoacrylonitrile 2c6 to substituted 1-acetonaphthalones 1d-i. The type of addition, [2+2]- vs. [4+2] is dependent on the location and nature of any additional substituent on the ring. In the case of the 4-bromo and 4-chloro derivatives 1b,c, only photosubstitution of bromine and chlorine by the 2-cyano-2-morpholinovinyl group has been observed5, whereas 4-fluoro-1-acetonaphthone 1d gave both photosubstitution and photoaddition products7.

The results of previous preparative scale experiments indicate the involvement of the π,π* triplet excited state of 1a,d-i in the reaction, because in the case of 1a, the starting material consumption is suppressed by addition of tetramethylidiazetine dioxide 6, a well known low energy triplet quencher8,9 incapable of undergoing any reactions with the excited carbonyl compounds.

1H NMR monitoring during irradiation of 1f in the presence of 2a and 1,3,5-hexatriene 7 as quencher revealed that 6×10⁻² M of 7 almost completely suppressed the formation of 4f from 1f and 2a (2×10⁻² M each) in acetonitrile solution.

In earlier work we reported on the observation of the lowest triplet excited state of naphthalene carbonyl compounds, which could be quenched by various captodative olefins of our interest10. Now we would like to report on such observations for substituted 1-acetonaphthalones 1b-i after 10 ns flash excitation and on rate constants of quenching of these triplets by two captodative olefins (2a, 2c) and the well known triplet quenchers 6 and 7.

Results and Discussion

Transient absorption spectra of substituted 1-acetonaphthalones 1b-i in acetonitrile or benzene solutions were obtained within 10 ns after excitation with the 354 nm pulse from a Nd-laser. Purging of solutions with argon increased the lifetime of the lowest triplet excited state under observation. T-T absorption maxima of 1-acetonaphthone 1a and its 2- or 4-substituted derivatives 1b-i and also the rate
constant for quenching by oxygen and other quenchers are shown in Table I.

The rate constants for quenching of triplet 1b-i by alkenes 2a,c, compound 6 and 1,3,5-hexatriene 7 have been extracted from Stern-Volmer plots of quenching of the T-T absorption. Representative examples are shown in the inset of figure 1 for quenching of 1d by 2a and 2c.

The data contained in Table 1 indicate that the triplet state of 1b-i is not only quenched by oxygen, but also by alkenes 2a, 2c, 6 and 7. This lends support to the involvement of triplet excited states of the ketones 1a-i in the photocycloaddition.

The observed rate constants for quenching of the triplet state of 1b-i by 2a and 2c in benzene are approximately two orders of magnitude lower than the diffusional limit (1.1 × 10^10 M^{-1}s^{-1}). Rate constants for the quenching of phosphorescence of 1b close to the diffusion controlled limit have been observed for pyrene, anthracene and tetracyanoethylene as quenchers in benzene (7.3 × 10^9, 9 × 10^9 and 3.2 × 10^9 M^{-1}s^{-1}, respectively)\(^\text{12}\). For alkenes 2a,c as quenchers the question for the mechanism of quenching seems justified. The liberation of halide ions from 1b,c suggests that at least for these ketones the quenching by 2a,c has an electron transfer component (1\(^\text{st}\) I.P. for 2a: 8.68 eV\(^\text{13}\)).
Table 1—T-T absorption maxima (354 nm excitation) and triplet quenching constants for acetonaphthones 1a-i

<table>
<thead>
<tr>
<th>Acetonaphthone</th>
<th>T-T λ&lt;sub&gt;max&lt;/sub&gt;/nm</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(O&lt;sub&gt;2&lt;/sub&gt;)</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(2a)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(2a)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(2c)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(6)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>k&lt;sub&gt;d&lt;/sub&gt;(7)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>490</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>≤380,470</td>
<td>15</td>
<td>0.41</td>
<td>0.53</td>
<td>4.37</td>
<td>41</td>
<td>63</td>
</tr>
<tr>
<td>1c</td>
<td>450</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>475</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>≤370,510</td>
<td>18</td>
<td>0.63</td>
<td>1.3</td>
<td>40</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>370,540</td>
<td>20</td>
<td>0.8</td>
<td>0.9</td>
<td>4.63</td>
<td>30</td>
<td>51</td>
</tr>
<tr>
<td>1g</td>
<td>460,525</td>
<td>16</td>
<td>0.84</td>
<td>2.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>≤380,500</td>
<td>20</td>
<td>0.57</td>
<td>0.55</td>
<td>1.98</td>
<td>31</td>
<td>49</td>
</tr>
<tr>
<td>1i</td>
<td>430,525</td>
<td>20</td>
<td>1.23</td>
<td>3.11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> in benzene; <sup>b</sup> in acetonitrile; <sup>c</sup> in methanol

Figure 1—Transient absorption spectra of 1d in argon-saturated acetonitrile in the presence of 2a (0.01 M) at 10 ns (○), 50 ns (●) and 200 ns (△) after the pulse; inset: dependences of the inverse triplet lifetime as a function of the concentration of 2a (●) and 2c (○).

The formation of a diradical intermediate, at least for the 1,4-addition, has been proposed due to the envisaged stabilization of one radical center by the so-called captodative effect<sup>1</sup>. On the other hand, the influence of additional substituents on the ring of 1b-i with this type of observed cycloaddition needs to be taken into account. For this reason, we tried to detect the formation of any transients originating from quenching of 1b-i by 2a and 2c. Transient absorption spectra of 1b-i in the presence of 2a or 2c (~20-75 mM) do not show any formation of a new absorption at λ> 380 nm, which does not support the formation of diradical- or exciplex intermediates absorbing in the accessible wavelength range. As representative example the transient absorption spectra of 1d in the presence of 2a are shown in Figure 1. Quenching of the triplet state of 1d by 2a only increases the inverse triplet lifetime, but does not alter the spectrum.

Experimental Section

Spectrograde solvents—acetonitrile, benzene and methanol (Merck “Uvasol”)- were used as received in all experiments. Starting materials were prepared
according to published procedures: substituted 1-acetonaphthones Ib-i'4-17, 2-morpholinoacrylonitrile 2a-8, 2-piperidinoacrylonitrile 2c-9, 3,3,4,4-tetramethyldiazetine dioxide 6-8, 1,3,5-hexatriene 7 as a mixture of isomers; 96% (GC) and stabilized with 0.2 % hydroquinone (Fluka) was used as received. Laser flash photolysis was carried out as described in previous work20. Solutions used for transient absorption measurements had an absorbance of 0.5 - 2 at 354 nm and were deaerated by purging with argon and measured at 24°C.

Acknowledgment

H. R. Memarian is indebted to the German Academic Exchange Service (DAAD) for a scholarship during the period July-August 1998.

References

7 Memarian H R, Nasr-Esfahani M & Döpp D, to be published separately.
17 Schneider W & Kunan F, Ber d chem Ges, 54, 1921, 2302.