(C(CH₃)=CH₂)CHOO (Z- and E-) + hν → products

Primary photochemical transitions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C(CH₃)=CH₂)CHOO + hν → CH₂=CH(CH₃)CO + O(³P)</td>
<td>(1)</td>
</tr>
<tr>
<td>→ CH₂=CH(CH₃)CO + O(¹D)</td>
<td>(2)</td>
</tr>
</tbody>
</table>

Absorption cross-section data

<table>
<thead>
<tr>
<th>Wavelength range/nm</th>
<th>Reference</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>315-500</td>
<td>Vansco et al., 2019</td>
<td>(a)</td>
</tr>
</tbody>
</table>

Comments

(a) Methacrolein oxide, (C(CH₃)=CH₂)CHOO, was prepared by PLP (248 nm) of (Z/E)-1,3-diiodobut-2-ene in O₂/Ar mixtures in a capillary tube. The photoproducts were cooled in a supersonic expansion and passed to a TOF mass spectrometer where they were ionised with VUV radiation at 118 nm. The UV absorption spectrum was determined from depletion of the m/z = 86 photo-ionisation signal resulting from excitation of the Π* ← Π transition of ground state (C(CH₃)=CH₂)CHOO molecules by tunable UV radiation (305 – 480 nm). The UV-induced depletion increased linearly with UV power and an absorption cross section at 380 nm of approximately 3 × 10⁻¹⁸ cm² molecule⁻¹ was estimated.

Preferred Values

Absorption cross-sections at 298 K relative to value at 380 nm

<table>
<thead>
<tr>
<th>λ/nm</th>
<th>σ/σ₃₈₀nm</th>
<th>λ/nm</th>
<th>σ/σ₃₈₀nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>0.886</td>
<td>410</td>
<td>0.823</td>
</tr>
<tr>
<td>330</td>
<td>0.850</td>
<td>420</td>
<td>0.759</td>
</tr>
<tr>
<td>340</td>
<td>0.749</td>
<td>430</td>
<td>0.672</td>
</tr>
<tr>
<td>350</td>
<td>0.749</td>
<td>440</td>
<td>0.471</td>
</tr>
<tr>
<td>360</td>
<td>0.886</td>
<td>450</td>
<td>0.466</td>
</tr>
<tr>
<td>370</td>
<td>0.938</td>
<td>460</td>
<td>0.270</td>
</tr>
<tr>
<td>380</td>
<td>1.000</td>
<td>470</td>
<td>0.249</td>
</tr>
<tr>
<td>390</td>
<td>0.957</td>
<td>480</td>
<td>0.170</td>
</tr>
<tr>
<td>400</td>
<td>0.883</td>
<td>490</td>
<td>0.098</td>
</tr>
</tbody>
</table>
Quantum Yields

\[ \phi_1 = 1.0 \text{ for } 315 < \lambda < 500 \text{ nm.} \]

Comments on Preferred Values

The only reported study of UV absorption spectrum of the methacrolein oxide Criegee intermediate, \((\text{C(CH}_3\text{)}=\text{CH}_2)\text{CHOO}\), was obtained by Vansco et al. (2019). The UV photodissociation action spectrum technique was used to record the spectrum of a mixture of the four conformers of \((\text{C(CH}_3\text{)}=\text{CH}_2)\text{CHOO}\) (i.e. two rotamers of each of Z- and E- \((\text{C(CH}_3\text{)}=\text{CH}_2)\text{CHOO}\)). The spectrum in the range 315-500 nm was broad with structured at wavelengths > 400 nm with a maximum at 380 nm which was estimated to be approximately 3 \( \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1} \). In light of the rough estimate no recommendation is given for the absolute absorption cross sections, but the shape of the spectrum is indicated in the table above. Absorption at \( \lambda < 500 \text{ nm} \) leads to rapid dissociation to methacrolein and \( \text{O}^{(1}\text{D}) \) atoms which were detected using 2 + 1 REMPI. The photodissociation quantum yields are likely to be close to unity.

References


Absorption spectrum of \((\text{C(CH}_3\text{)}=\text{CH}_2)\text{CHOO}\), Z- and E- conformers not resolved, from Figure 4 in Vansco et al. (2019).