IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet P20

This data sheet updated: 16th May 2002.

$CH_3O_2NO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2$	(1)	86	1391
$\rightarrow CH_3O + NO_3$	(2)	135	886

[a]Only approximate values of $\Delta H°_{298}$ values are given since the heat of formation of $CH_3O_2NO_2$ is not well known.

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202-280	Bridier, Lesclaux and Veyret, 1992[1]	(a)

Comments

(a) Flash photolysis of Cl_2 in the presence of CH_4-O_2-NO_2 mixtures at a total pressure of 1 bar, with UV absorption to monitor the concentrations of CH_3O_2 radicals and $CH_3O_2NO_2$.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\ \sigma$/cm^2	λ/nm	$10^{20}\ \sigma$/cm^2
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

In view of the thermal instability of $CH_3O_2NO_2$, the measurement of the cross-sections for $CH_3O_2NO_2$ presents considerable experimental problems. Nevertheless, the measurements of Bridier *et al*.[1] are in moderately good agreement with previous data[2-4] at wavelengths < 255 nm and are taken as the preferred values in the range 200 nm to 280 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall,[2] which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO_2NO_2.

There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the $-NO_2$ chromophore (for example, HNO_3), it is likely that absorption around 270 nm is associated with an orbitally forbidden n-π^* transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1 + \phi_2 = 1$.

References

1 I. Bridier, R. Lesclaux, and B. Veyret, Chem. Phys. Lett. **191**, 259 (1992).

2 R. A. Cox and G. S. Tyndall, Chem. Phys. Lett. **65**, 357 (1979).

3 O. Morel, R. Simonaitis, and J. Heicklen, Chem. Phys. Lett. **73**, 38 (1980).

4 S. P. Sander and R. T. Watson, J. Phys. Chem. **84**, 1664 (1980).