IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P19

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$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow$ products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$2\text{-}C_4H_9ONO_2 + h\nu \rightarrow 2\text{-}C_4H_9O + NO_2$	(1)		
$\rightarrow CH_3COC_2H_5 + HONO$	(2)		
$\rightarrow 2\text{-}C_4H_9ONO + O$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250-320	Roberts and Fajer, 1989[1]	(a)

Comments

(a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single beam spectrophotometer with a photometric accuracy of ±0.5%. The expression for σ as a function of λ was derived from a least-squares fit to the data at λ ≥ 270 nm.

Preferred Values
Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
250	6.5	290	1.8
255	5.6	295	1.3
260	5.2	300	0.74
265	4.8	305	0.50
270	4.2	310	0.29
275	3.7	315	0.15
280	3.1	320	0.08
285	2.4		

Values at λ ≤265 nm are taken from graphs in ref. 1.
Values at λ ≥270 nm are calculated from the expression given in ref. 1 based on a least-squares fit to the data.

Comments on Preferred Values

The only available measurements of the absorption cross-sections are those of Roberts and Fajer.[1] Their measurements of cross-sections for other alkyl nitrates have agreed well with other studies, and their values are accepted as the preferred values for 2-butyl nitrate.

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 2-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight.[2] Thus the measured rate of formation of NO_2 matched well with the calculated rates of photolyses based on measurement of the absorption cross-sections, solar irradiances, and an assumed value of $\phi = 1$ throughout the wavelength region 290 nm to 330 nm.[2]

References

1. J. M. Roberts and R. W. Fajer, Environ. Sci. Technol. **23**, 945 (1989).
2. W. T. Luke, R. R. Dickinson, and L. J. Nunnermacker, J. Geophys. Res. **94**, 14905 (1989).