IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet P32

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4-methy-2-nitrophenol ($CH_3C_6H_3(OH)NO_2$) + hυ → products

Primary photochemical transitions

Reaction	$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(OH) + NO_2$ (1) $\rightarrow CH_3C_6H_3C_6H_4(O) + HONO$ (2)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
320 - 450	Chen et al., 2011	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ (HONO) = ~10^{-4}	320 – 480 (λ_{max} = 370)	Bejan et al.,2006	(b)

Comments

(a) Absorption cross sections of 2-nitrophenol, 3-methyl-2-nitrophenol, and 4-methyl-2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1 σ).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 4-methy-2-nitrophenol measured by FTIR and

of the HONO product by derivativisation on-line followed by LPAS. HONO formed but ϕ(HONO) was not determined.

Preferred Values

Absorption cross-sections for 4-methy-2-nitrophenol at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
320	0.352	363	0.829	407	0.022
321	0.403	364	0.798	408	0.018
322	0.458	365	0.775	409	0.014
323	0.559	366	0.744	410	0.011
324	0.653	367	0.713	411	0.008
325	0.666	368	0.688	412	0.007
326	0.725	369	0.662	413	0.004
327	0.735	370	0.640	414	0.003
328	0.763	371	0.623	415	0.001
329	0.782	372	0.598	416	0.002
330	0.782	373	0.581	417	0.001
331	0.818	374	0.564	418	-0.001
332	0.831	375	0.543	419	-0.002
333	0.860	376	0.525	420	-0.004
334	0.866	377	0.505	421	-0.004
335	0.899	378	0.487	422	-0.005
336	0.912	379	0.470	423	-0.005
337	0.946	380	0.451	424	-0.007
338	0.964	381	0.425	425	-0.007
339	0.995	382	0.402	426	-0.006
340	1.022	383	0.374	427	-0.007
341	1.010	384	0.351	428	-0.008
342	1.006	385	0.319	429	-0.009
343	1.015	386	0.288	430	-0.009
344	1.005	387	0.259	431	-0.009
345	1.001	388	0.231	432	-0.009
346	1.012	389	0.204	433	-0.009
347	1.017	390	0.177	434	-0.009
348	1.005	391	0.153	435	-0.009
349	1.015	392	0.134	436	-0.009
350	1.022	393	0.116	437	-0.007
351	1.011	394	0.102	438	-0.006
352	1.021	395	0.089	439	-0.006
353	1.026	396	0.081	440	-0.007
354	1.011	397	0.073	441	-0.006
355	1.007	398	0.065	442	-0.005
356	0.995	399	0.059	443	-0.005
357	0.977	400	0.054	444	-0.005
358	0.952	401	0.048	445	-0.006
359	0.927	402	0.045	446	-0.005
360	0.901	403	0.041	447	-0.005
361	0.877	404	0.035	448	-0.006
362	0.850	405	0.031	449	-0.006
		406	0.027	450	-0.005

Quantum Yields

No recommendation

Comments on Preferred Values

The recommended cross sections for 4-methy-2-nitrophenol are those reported by Chen et al. (2011) These appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption of 4-methy-2-nitrophenol varied linearly with concentration and the resulting spectra are shown in Figure 1. The absorption band of 4-methy-2-nitrophenol peaks around 340-353 nm (absorption cross-section of 1.76×10^{-17} $cm^2 molecule^{-1}$), which is blue-shifted by ~30 nm from the solution spectra recorded in acetonitryl (Bardini, PhD thesis, University of Cork, Ireland, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) $\rightarrow$ π^*(nitro group) transition.

The photolysis frequency reported by Bejan et al (2007) was approximately a factor of 2 slower than for 3-methy-2-nitrophenol. Values of ϕ(HONO) were not given.

References

Bejan, I., El Aal, Y.A., Barnes, I., Benter, T., Bohn, B., Wiesen, P. and J Kleffmann, J., *Phys. Chem. Chem. Phys*., 2006, 8, 2028–2035.

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., and Benter, Th., *Phys.Chem.Chem.Phys*., 2007, 9 5686-5692.

Bardini, PhD thesis, University of Cork, Ireland, 2006).

Chen, J., Wenger, J.C., and Venables, D.S., *J. Phys. Chem. A*, 2011, 115 12235-12242.

Figure 1 Absorption spectrum of 4-methy-2-nitrophenol in the gas phase.