IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P31

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3-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) = 1.5 x 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% (1σ).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 3-methy-2-nitrophenol measured by FTIR and of the HONO product by derivatisation on-line followed by LPAS. Value of ϕ(HONO) was

estimated from photolysis rate and absorbed intensity calculated from the solution phase spectrum of 3-methy-2-nitrophenol.

Preferred Values

Absorption cross-sections for 3-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	0.454	363	0.553	407	0.035
321	0.544	364	0.533	408	0.033
322	0.615	365	0.512	409	0.030
323	0.637	366	0.494	410	0.028
324	0.690	367	0.476	411	0.025
325	0.717	368	0.455	412	0.022
326	0.734	369	0.439	413	0.021
327	0.756	370	0.425	414	0.019
328	0.753	371	0.407	415	0.019
329	0.770	372	0.388	416	0.016
330	0.779	373	0.379	417	0.015
331	0.795	374	0.370	418	0.013
332	0.797	375	0.356	419	0.013
333	0.812	376	0.345	420	0.012
334	0.829	377	0.333	421	0.012
335	0.828	378	0.323	422	0.012
336	0.841	379	0.313	423	0.010
337	0.847	380	0.296	424	0.001
338	0.849	381	0.280	425	0.009
339	0.847	382	0.264	426	0.008
340	0.843	383	0.248	427	0.008
341	0.842	384	0.231	428	0.007
342	0.842	385	0.215	429	0.008
343	0.832	386	0.196	430	0.008
344	0.823	387	0.181	431	0.009
345	0.812	388	0.166	432	0.008
346	0.803	389	0.148	433	0.009
347	0.797	390	0.135	434	0.010
348	0.786	391	0.122	435	0.008
349	0.778	392	0.109	436	0.009
350	0.768	393	0.099	437	0.009
351	0.763	394	0.089	438	0.010
352	0.750	395	0.081	439	0.010
353	0.739	396	0.073	440	0.010
354	0.729	397	0.068	441	0.008
355	0.720	398	0.063	442	0.007
356	0.708	399	0.059	443	0.008
357	0.686	400	0.056	444	0.009
358	0.663	401	0.052	445	0.008
359	0.640	402	0.049	446	0.008
360	0.618	403	0.045	447	0.008
361	0.594	404	0.043	448	0.007
362	0.572	405	0.040	449	0.006
		406	0.037	450	0.006

Quantum Yields

No recommendation

Comments on Preferred Values

The recommended cross sections for 3-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 3-methy-2-nitrophenol varied linearly with concentration and the resulting spectra are shown in Figure 1. The absorption band of 3-methy-2-nitrophenol peaks around 336 - 339 nm (absorption cross-section of 1.76×10^{-17} $cm^2 molecule^{-1}$), which is blue-shifted by ~ 20 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.

Bejan et al (2006) showed that HONO was a direct product of photolysis. However the value of ϕ(HONO) reported by Bejan et al (2006) is likely to be underestimated since it was based on absorbed light intensity calculated from the solution phase spectrum of 3-methy-2-nitrophenol, which Chen et al. (2011) show is redshifted compared to the gas phase.

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 3-methy-2-nitrophenol in the gas phase.