IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet P28

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2-nitrophenol ($C_6H_4(OH)NO_2$) + hυ → products

Primary photochemical transitions

Reaction		$\Delta H°_{298}$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_6H_4(OH)NO_2 \rightarrow C_6H_4(OH) + NO_2$	(1)		
$\rightarrow C_6H_4(O) + HONO$	(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) = 1.15 x 10^{-2}	320 – 480 (λ_{max} = 370)	Chen et al., 2011	(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 s).

(b) Chen et al (2011) recalculated the quantum yield based on photolysis rates observed by Bardini (2006) under defined conditions in the EUPHORE chamber facility (Valencia, Spain), using their new gas phase cross-sections.

Preferred Values

Absorption cross-sections for 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	0.926	363	0.731	407	0.010
321	1.084	364	0.680	408	0.009
322	1.219	365	0.635	409	0.008
323	1.353	366	0.592	410	0.008
324	1.437	367	0.555	411	0.007
325	1.522	368	0.522	412	0.007
326	1.578	369	0.492	413	0.007
327	1.600	370	0.465	414	0.006
328	1.602	371	0.439	415	0.006
329	1.596	372	0.412	416	0.006
330	1.604	373	0.387	417	0.006
331	1.606	374	0.363	418	0.005
332	1.628	375	0.340	419	0.005
333	1.641	376	0.312	420	0.005
334	1.650	377	0.282	421	0.005
335	1.662	378	0.250	422	0.005
336	1.681	379	0.225	423	0.004
337	1.675	380	0.203	424	0.004
338	1.680	381	0.183	425	0.004
339	1.675	382	0.163	426	0.003
340	1.656	383	0.144	427	0.003
341	1.630	384	0.128	428	0.003
342	1.593	385	0.113	429	0.003
343	1.552	386	0.101	430	0.003
344	1.518	387	0.091	431	0.003
345	1.483	388	0.081	432	0.003
346	1.454	389	0.072	433	0.003
347	1.425	390	0.063	434	0.003
348	1.395	391	0.056	435	0.003
349	1.361	392	0.050	436	0.003
350	1.327	393	0.043	437	0.003
351	1.300	394	0.038	438	0.003
352	1.273	395	0.034	439	0.003
353	1.248	396	0.031	440	0.003
354	1.221	397	0.028	441	0.003
355	1.182	398	0.025	442	0.003
356	1.132	399	0.022	443	0.003
357	1.072	400	0.020	444	0.003
358	1.006	401	0.018	445	0.003
359	0.942	402	0.016	446	0.003
360	0.883	403	0.014	447	0.003
361	0.830	404	0.013	448	0.003
362	0.779	405	0.011	449	0.003
		406	0.011	450	0.003

Quantum Yields

No recommendation

Comments on Preferred Values

The recommended cross sections for 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 2-nitrophenol varied linearly with concentration and the resulting spectra are shown in Figure 1. The absorption band of 2-nitrophenol peaks around 336 - 339 nm (absorption cross-section of 1.76 x 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.

The value of ϕ(HONO) recalculated by Chen et al (2011) from the measurements of Bardini (2006) in the EUPHORE chamber facility (Valencia, Spain), is substantially higher than earlier estimates e.g by Bejan et al. (2006), which were based on absorbed light intensity calculated from the solution phase spectrum of 2-nitrophenol, which is redshifted compared to the gas phase. the quantum yield based on photolysis rates observed by under defined conditions. The value of ϕ(HONO) = 1.15 x 10^{-2} could be used in atmospheric modelling, but experimental uncertainties preclude a safe recommendation.

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 2-nitrophenol in the gas phase.