

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet PNOx5

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### NO<sub>3</sub> + hv → products

#### Primary photochemical transitions

Reaction		$\Delta H^\circ/\text{kJ mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
NO <sub>3</sub> + hv → NO + O <sub>2</sub> ( <sup>3</sup> Σ)	(1)	10.8	11080
→ NO + O <sub>2</sub> ( <sup>1</sup> Δ)	(2)	105	1139
→ NO + O <sub>2</sub> ( <sup>1</sup> Σ)	(3)	168	714
→ NO <sub>2</sub> + O( <sup>3</sup> P)	(4)	204	587

#### Absorption cross-section data

Wavelength range/nm	Reference	Comments
400-700	Sander, 1986 <sup>1</sup>	(a)

#### Quantum yield data

Measurement	Wavelength/nm	Reference	Comments
$\phi(\text{NO}+\text{O}_2)$ , $\phi_i$	570-635	Orlando <i>et al.</i> , 1993 <sup>2</sup>	(b)

#### Comments

- (a) Two methods were used to produce NO<sub>3</sub>. In one, NO<sub>3</sub> radicals were generated from the flash photolysis of Cl<sub>2</sub>-ClONO<sub>2</sub> mixtures, with NO<sub>3</sub> formation and ClONO<sub>2</sub> loss being monitored by UV absorption. Measurements were made at 230, 250, and 298 K. The value of  $\sigma(\text{NO}_3)$  at 662 nm and 298 K, determined by this method ( $2.28 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ ), was preferred by the author. The cross section was observed to increase as the temperature was lowered. NO<sub>3</sub> was also produced in a discharge flow system by the F+HNO<sub>3</sub> reaction. The value of  $\sigma(\text{NO}_3)$  at 662 nm and 298 K determined by this method was  $1.83 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ . Values of  $\sigma(\text{NO}_3)$  were tabulated for 1nm intervals from 400 nm to 700 nm for 298 K and 230 K.

(b) The photodissociation of  $\text{NO}_3$  was studied at 298 K using pulsed laser photolysis, with resonance fluorescence detection of  $\text{O}(^3\text{P})$  atoms and  $\text{NO}(X^2\Pi)$ .  $\phi[\text{O}(^3\text{P})]$  was 1.0 over the range 570-585 nm, decreasing to a value of  $< 0.1$  at 635 nm.  $\phi(\text{NO})$  was  $< 0.1$  at 580 nm and about  $0.20 \pm 0.1$  at 590 nm. These data were combined with earlier results of Magnotta and Johnston<sup>3</sup> to provide quantum yields of  $\phi(\text{NO}+\text{O}_2)$  and  $\phi(4)$  as a function of wavelength (586-639 nm) and to calculate photolysis rates for overhead Sun at the earth's surface, with  $J(\text{NO}_2+\text{O}) = 0.19 \text{ s}^{-1}$  and  $J(\text{NO}+\text{O}_2) = 0.016 \text{ s}^{-1}$ .

### Preferred Values

#### Absorption cross-sections of $\text{NO}_3$ at 298 K and 230 K.

$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$
	$\text{m}^2$							
	298 K	230 K		298 K	230 K		298 K	230 K
400	0.0	0.4	431	1.3	1.8	462	4.0	4.0
401	0.0	0.4	432	1.5	1.8	463	4.1	4.8
402	0.0	0.5	433	1.8	2.0	464	4.8	5.1
403	0.2	0.5	434	1.8	2.2	465	5.1	5.4
404	0.0	0.3	435	1.6	2.4	466	5.4	5.7
405	0.3	0.7	436	1.5	2.3	467	5.7	6.0
406	0.2	0.6	437	1.8	2.0	468	5.6	5.9
407	0.1	0.5	438	2.1	2.2	469	5.8	6.0
408	0.3	0.5	439	2.0	2.8	470	5.9	5.7
409	0.0	0.8	440	1.9	2.4	471	6.2	6.2
410	0.1	0.5	441	1.8	2.5	472	6.4	6.5
411	0.2	0.8	442	2.1	2.3	473	6.2	6.5
412	0.5	0.4	443	1.8	2.3	474	6.2	6.4
413	0.5	0.7	444	1.9	2.4	475	6.8	7.4
414	0.2	1.2	445	2.0	2.9	476	7.8	8.3
415	0.6	0.8	446	2.4	2.9	477	7.7	8.2
416	0.6	0.8	447	2.9	3.3	478	7.3	7.4
417	0.7	1.1	448	2.4	3.6	479	7.3	7.4
418	0.5	1.1	449	2.8	3.3	480	7.0	7.5
419	0.8	1.1	450	2.9	3.3	481	7.1	7.4
420	0.8	1.4	451	3.0	3.7	482	7.1	7.3
421	0.8	1.3	452	3.3	4.0	483	7.2	7.1
422	0.9	1.3	453	3.1	3.7	484	7.7	7.4
423	1.1	1.3	454	3.6	4.0	485	8.2	8.2
424	0.9	1.4	455	3.6	4.1	486	9.1	9.5
425	0.7	1.7	456	3.6	3.6	487	9.2	9.4
426	1.4	1.6	457	4.0	4.2	488	9.5	9.2
427	1.4	1.3	458	3.7	4.7	489	9.6	10.6
428	1.2	1.6	459	4.2	4.5	490	10.3	11.2
429	1.1	1.4	460	4.0	4.6	491	9.9	10.3
430	1.7	1.7	461	3.9	4.3	492	9.9	10.6

$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$
	$\text{m}^2$							
	298 K	230 K		298 K	230 K		298 K	230 K
493	10.1	10.9	538	23.4	26.0	583	29.3	34.6
494	10.1	10.1	539	20.4	22.4	584	28.2	32.8
495	10.6	11.1	540	21.0	22.6	585	28.9	34.0
496	12.1	12.9	541	20.4	21.8	586	33.2	39.7
497	12.2	14.0	542	18.8	19.7	587	41.6	51.8
498	12.0	13.2	543	16.8	17.5	588	50.4	63.8
499	11.7	12.6	544	17.0	17.3	589	61.3	77.3
500	11.3	12.3	545	19.6	21.3	590	59.6	71.8
501	11.1	11.4	546	24.2	26.5	591	54.4	64.6
502	11.1	11.1	547	29.1	33.0	592	51.1	60.2
503	11.1	11.9	548	29.8	33.4	593	45.8	53.2
504	12.6	13.3	549	27.1	29.7	594	41.9	50.2
505	12.8	14.0	550	24.8	27.8	595	42.9	52.8
506	13.4	15.0	551	24.3	27.6	596	46.2	58.1
507	12.8	14.0	552	24.7	28.5	597	43.6	54.0
508	12.7	13.0	553	25.3	29.4	598	36.7	43.7
509	13.5	14.1	554	27.8	33.1	599	31.0	36.5
510	15.1	16.5	555	31.1	38.0	600	27.6	29.7
511	17.3	20.0	556	32.6	39.2	601	28.6	30.4
512	17.7	21.1	557	32.9	39.3	602	33.2	35.7
513	16.0	19.2	558	35.1	42.2	603	38.0	43.0
514	15.8	17.3	559	37.2	45.3	604	43.7	51.4
515	15.8	17.0	560	33.2	38.5	605	43.6	53.2
516	15.6	17.5	561	29.8	33.8	606	33.2	39.6
517	14.9	15.4	562	29.0	32.7	607	24.0	26.5
518	14.4	14.9	563	28.0	32.1	608	18.5	19.1
519	15.4	15.9	564	27.2	30.8	609	17.1	17.7
520	16.8	17.3	565	27.3	31.0	610	17.7	18.5
521	18.3	18.9	566	28.5	33.0	611	19.1	20.7
522	19.3	20.6	567	28.1	31.4	612	22.3	25.2
523	17.7	19.1	568	28.5	32.0	613	26.3	32.0
524	16.4	16.8	569	28.9	32.6	614	25.5	30.5
525	15.8	16.0	570	27.9	31.1	615	22.6	25.8
526	16.3	16.8	571	27.6	30.9	616	20.9	22.5
527	18.1	19.3	572	27.4	30.5	617	21.1	22.0
528	21.0	23.8	573	27.8	30.9	618	23.9	24.4
529	23.9	27.3	574	28.6	31.9	619	25.6	27.1
530	22.3	24.7	575	30.8	36.0	620	32.7	35.8
531	20.9	22.7	576	32.7	38.7	621	52.4	62.9
532	20.2	22.0	577	33.8	39.5	622	101.8	121.3
533	19.5	21.1	578	33.1	38.5	623	147.3	174.5
534	20.4	22.7	579	32.4	38.3	624	120.5	138.7
535	23.0	26.6	580	33.4	39.9	625	83.8	100.7
536	25.7	30.6	581	35.5	43.9	626	73.0	88.2
537	25.8	30.5	582	32.8	39.5	627	75.3	96.1

$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$	$\lambda/\text{nm}$	$10^{19}\sigma/\text{cm}^2$	$10^{19}\sigma/\text{cm}^2$
	$\text{m}^2$							
	298 K	230 K		298 K	230 K		298 K	230 K

628	73.7	94.3	649	5.4	5.3	670	9.5	11.2
629	69.8	90.3	650	5.0	5.0	671	7.9	9.4
630	67.6	89.7	651	5.5	5.6	672	7.6	9.7
631	48.4	61.0	652	6.1	6.6	673	6.4	8.1
632	32.7	39.8	653	7.1	7.9	674	5.2	6.3
633	21.7	25.1	654	8.2	9.2	675	4.8	5.5
634	16.4	17.3	655	9.8	11.0	676	4.9	5.2
635	14.4	14.0	656	13.3	14.4	677	5.9	6.2
636	16.9	16.2	657	17.1	18.5	678	7.5	7.2
637	20.7	20.1	658	24.2	25.9	679	7.8	7.3
638	20.3	18.9	659	40.7	42.7	680	6.9	6.4
639	15.8	14.2	660	74.5	79.0	681	5.3	5.3
640	12.3	11.3	661	144.8	167.5	682	4.0	4.4
641	10.0	9.5	662	210.0	266.9	683	3.0	3.2
642	9.2	8.4	663	174.4	229.7	684	2.6	2.8
643	9.7	8.1	664	112.9	145.5	685	1.8	2.4
644	9.5	8.4	665	74.1	92.9	686	1.6	1.5
645	8.6	8.0	666	49.6	62.9	687	1.2	2.3
646	7.5	6.9	667	30.4	37.4	688	1.2	2.0
647	7.0	6.8	668	19.0	23.3	689	1.2	1.9
648	6.2	6.3	669	12.5	14.5	690	1.0	2.1

### Quantum Yields at 298 K

$\phi_4 = 1.0$  for  $\lambda \leq 587$  nm.

#### Comments on Preferred Values

The preferred values of the absorption cross-sections are based on the data of Sander<sup>1</sup> and are obtained by normalizing the experimental values of Sander<sup>1</sup> in the range 400-691 nm to the value of  $2.1 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> for the peak value at 662 nm. This peak value is adopted from the evaluation of Wayne *et al.*<sup>4</sup> The measurements of Yokelson *et al.*,<sup>5</sup> made over the range 440-720 nm, which supersede previous data from the same laboratory,<sup>6</sup> are in good agreement with the data of Sander.<sup>1</sup>

There is also good agreement between the studies of Sander<sup>1</sup> and of Yokelson *et al.*<sup>5</sup> on the temperature dependence of the cross-sections, which were studied over the range 230-298 K by Sander,<sup>1</sup> and 200-298 K by Yokelson *et al.*<sup>5</sup> A significant increase in cross-section is found as temperature is lowered, in contrast to the findings of Cantrell *et al.*,<sup>7</sup> who found temperature change to have little effect. To obtain the temperature dependence of the band at 662 nm, the value of  $\sigma$  at 230 K obtained by Sander<sup>1</sup> is accepted and combined with the preferred value at 298 K to give  $\sigma(T) = \{4.59 \times 10^{-17} - (8.37 \times 10^{-20} T)\}$  cm<sup>2</sup> molecule<sup>-1</sup> at 662 nm.

The measurements of Orlando *et al.*<sup>2</sup> confirm qualitatively the wavelength dependence of  $\phi(\text{NO} + \text{O}_2)$  and  $\phi_4$  observed in the earlier room temperature measurements of Magnotta and Johnston,<sup>3</sup> and provide more accurate values for  $\phi_4$ . The earlier problem<sup>3</sup> of quantum yields in excess of 1.4 was not encountered in the work of Orlando *et al.*<sup>2</sup> which confirms that NO<sub>3</sub> radical dissociation is exclusively to NO<sub>2</sub> + O(<sup>3</sup>P) at wavelengths less than 587 nm.

A molecular beam study of Davis *et al.*<sup>8</sup> has provided considerable insight into the photodissociation of the NO<sub>3</sub> radical. There is a very sharp threshold for channel (4) at 587 nm for cold NO<sub>3</sub> and any dissociation at longer wavelengths via channel (4) must occur from internally excited NO<sub>3</sub>. At  $\lambda \geq 588$  nm this process competes with photodissociation of NO<sub>3</sub> to form NO + O<sub>2</sub> via a three-centre transition state from the vibrationally excited ground state. The yield from this process falls off above 600 nm and may only occur from hot band absorption above 605 nm. These facts imply that the branching ratio for bulk, thermally equilibrated NO<sub>3</sub> radicals will

depend very strongly on temperature, especially near the threshold for the NO<sub>2</sub>-forming channel, where higher temperatures will tend to favour the simple bond fission, channel (4).

Using the measured energy thresholds from the molecular beam experiments, Johnston *et al.*<sup>9</sup> have modelled product yields from the excited NO<sub>3</sub> resulting from photon absorption. They have calculated values of  $\phi(\text{NO})$ ,  $\phi(\text{NO}_2)$ , and  $\phi(\text{fluorescence})$  as a function of wavelength in the range 401-690 nm at temperatures of 190, 230, and 298 K. The values at 298 K agree well with the experimental findings of Orlando *et al.*<sup>2</sup> with only some departures for  $\phi(\text{NO}_2)$  in the 605-620 nm region.

On the basis of their measured quantum yields, Orlando *et al.*<sup>2</sup> have suggested photodissociation rates at the earth's surface, for an overhead sun, and the wavelength range 400-700 nm, of  $J(\text{NO}_2 + \text{O}) = 0.19 \text{ s}^{-1}$  and  $J(\text{NO} + \text{O}_2) = 0.016 \text{ s}^{-1}$ . These are preferred for atmospheric calculations. The experimental values of Magnotta and Johnston<sup>3</sup> are in agreement, and the calculations of Johnston *et al.*<sup>9</sup> also provide support for these photodissociation rates.

The information from the molecular beam experiments of Davis *et al.*<sup>8</sup> dictates that these values of  $J$  only apply for temperatures close to room temperature. Calculated values are available for lower temperatures, but further measurements of the quantum yields for NO<sub>3</sub> radical photolysis in bulk samples at lower temperatures are required before recommendations can be made for atmospheric photolysis rates at stratospheric temperatures.

## References

- <sup>1</sup> S. P. Sander, *J. Phys. Chem.* **90**, 4135 (1986).
- <sup>2</sup> J. J. Orlando, G. S. Tyndall, G. K. Moortgat, and J. G. Calvert, *J. Phys. Chem.* **97**, 10996 (1993).
- <sup>3</sup> F. Magnotta and H. S. Johnston, *Geophys. Res. Lett.* **7**, 769 (1980).
- <sup>4</sup> R. P. Wayne, I. Barnes, P. Briggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, and H. Sidebottom, *Atmos. Environ.* **25A**, 1 (1991).
- <sup>5</sup> R. K. Yokelson, J. B. Burkholder, R. W. Fox, R. K. Talukdar, and A. R. Ravishankara, *J. Phys. Chem.* **98**, 13144 (1994).
- <sup>6</sup> A. R. Ravishankara and R. L. Mauldin III, *J. Geophys. Res.* **91**, 8709 (1986).
- <sup>7</sup> C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, *J. Phys. Chem.* **91**, 5858 (1987).
- <sup>8</sup> H. F. Davis, B. Kim, H. S. Johnston, and Y. T. Lee, *J. Phys. Chem.* **97**, 2172 (1993).
- <sup>9</sup> H. S. Johnston, H. S. Davis, and Y. T. Lee, *J. Phys. Chem.* **100**, 4713 (1996).