Fate of the $CHBr_2O$ radical in air

by
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Abstract

Trace amounts of bromoform ($CHBr_3$) in air have been photolyzed at 266 and 303 nm to form Br atoms and $CHBr_2$ radicals. The Br concentration as a function of time is followed by resonance fluorescence. The $CHBr_2$ radicals react with O_2 in the air to form peroxy radicals. When NO is added, the peroxy radicals react further with NO to form NO_2 and a dibromomethoxy radical, $CHBr_2O$. Evidence is presented that this $CHBr_2O$ radical is unstable, decomposing rapidly to CHBrO and a second Br atom. The rise time of this secondary Br signal can be used to derive several rate constants for this system. The amplitude of the secondary Br signal shows that all of the $CHBr_2O$ radicals decompose for the conditions used in these experiments.

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seaweed ----------> CH_3Br, CH_2Br_2, **$CHBr_3$**, $CHBr_2Cl$

$CHBr_3 + OH$ ----------> $CBr_3 + H_2O$

$CHBr_3 + h\nu$ ----------> $CHBr_2 + Br$

$CHBr_2 + O_2$ ----------> $CHBr_2O_2$

$CHBr_2O_2 + NO$ ----------> $CHBr_2O + NO_2$

$CHBr_2O \xrightarrow{O_2} CBr_2O + HO_2$

$CHBr_2O$? $\rightarrow CHBrO + Br$

The Experiment

$CHBr_3 + h\nu$ ----------> $CHBr_2$ + **Br** (1st Br atom)

$CHBr_2 + O_2$ ----------> $CHBr_2O_2$

$CHBr_2O_2 + NO$ ----------> $CHBr_2O + NO_2$

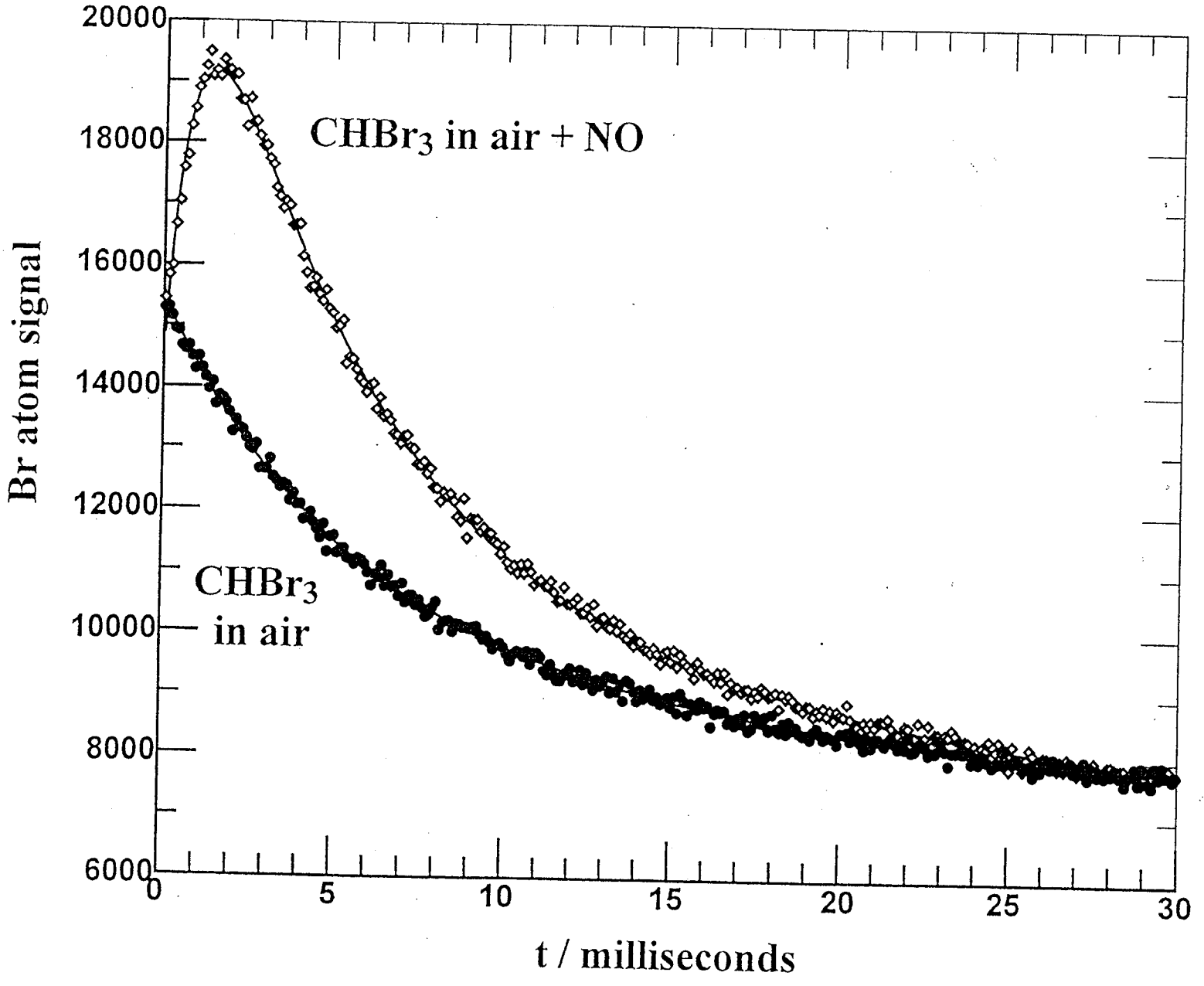
If: $CHBr_2O + O_2$ ----------> $CBr_2O + HO_2$ (no secondary Br)

or

If: $CHBr_2O$ ----------> $CHBrO$ + **Br** (2nd Br atom)

Equipment: A YAG laser was used at 266 nm with approximately 1 mJ/pulse at 3 Hz. The YAG was also used at 532 nm to pump a dye laser to generate 606 nm pulses, which were then doubled to give 303 nm, also about 1 mJ/pulse.

The resonance fluorescence system, consisting of a bromine resonance lamp (~10 watts, 180 MHz) and solar blind photomultiplier, was on loan from Prof. Darin Toohey of the Program in Atmospheric and Oceanic Sciences, University of Colorado, Boulder, Colorado. The output pulses were counted as a function of time on a multichannel scaler (Ortec MCS-pci).


20000
18000
16000
14000
12000
10000
8000
6000
Br atom signal
CHBr3 in air + NO
CHBr3
in air
0
5
10
15
20
25
30
t / milliseconds

Assumed Mechanism

[abbreviations: R = $CHBr_2$; RO_2 = $CHBr_2O_2$ and RO = $CHBr_2O$]

Initiation:

$$CHBr_3 + h\nu \;\text{------>}\; CHBr_2 + Br$$

Loss of $CHBr_2$:

$$CHBr_2 + O_2 \xrightarrow{k1a} CHBr_2O_2$$

$$CHBr_2 + NO \xrightarrow{k1b} CHBr_2NO$$

$$CHBr_2 \xrightarrow{k1c} \text{diffusional loss}$$

then solving for $CHBr_2$,

$$\mathbf{[CHBr_2] = [R] = S0\ exp(-K1\ t)}$$

where,

$$\mathbf{K1 = k1a[O_2] + k1b[NO] + k1c}$$

and

S0 = [Br] = [$CHBr_2$] immediately after the laser pulse

Loss of $CHBr_2O_2$:

$$CHBr_2O_2 + NO \xrightarrow{k2a} CHBr_2O + NO_2$$

$$CHBr_2O_2 \xrightarrow{k2c} \text{diffusional loss}$$

solving for $CHBr_2O_2$ as a function of time,

$$\mathbf{[RO_2] = k1a[O_2]S0\{\ exp(-K2\ t) - exp(-K1\ t)\ \}/(K1 - K2)}$$

$$\mathbf{K2 = k2a[NO] + k2c}$$

***Formation and loss of Br*:**

Will assume that every $CHBr_2O$ that is formed rapidly decomposes to Br and CHBrO (this assumption to be tested later):

$$CHBr_2O \xrightarrow{\text{fast}} CHBrO + Br$$

$$Br \xrightarrow{k3c} \text{diffusional loss}$$

$$d[Br]/dt = k2a[NO][RO_2] - K3[Br]$$

where, **K3 = k3c** (only loss process)

Solving this differential equation using the previous expression for $[RO_2]$, and the boundary condition that [Br] = S0 at time = 0, yields:

$$\mathbf{[Br] = S0\ exp(-K3\ t) + K1\ K2\ F1\ F2\ S0\ \{M2/(K2 - K3) - M1/(K1 - K3)\}/(K1 - K2)}$$

where **F1 = k1a[O2]/K1** = fraction of R that forms RO_2

F2 = k2a[NO]/K2 = fraction of RO_2 that forms RO, and thus gives a second Br atom

$$\mathbf{M1 = \{exp(-K3\ t) - exp(-K1\ t)\}}$$

$$\mathbf{M2 = \{exp(-K3\ t) - exp(-K2\ t)\}}$$

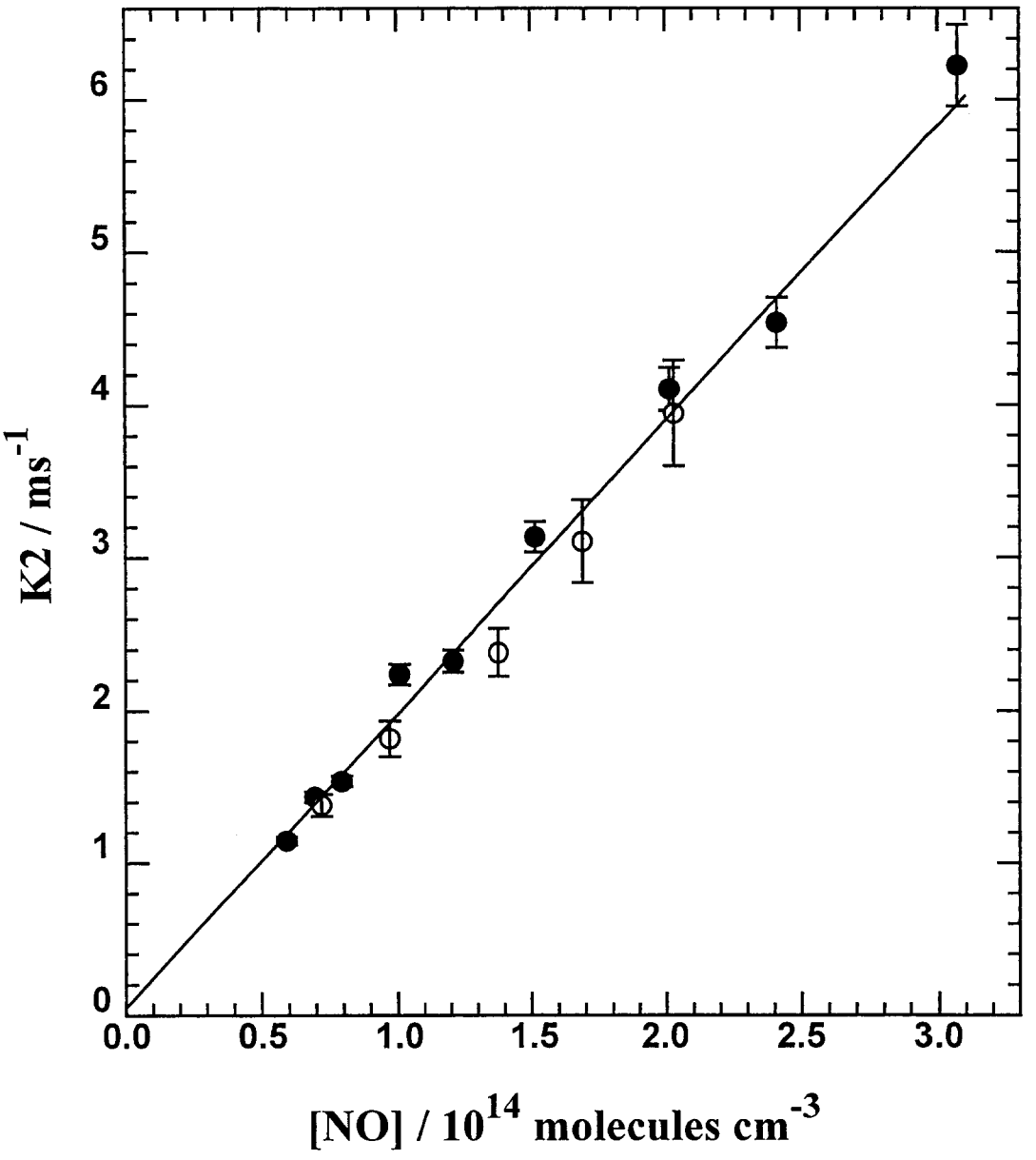
For fitting the experimental data, two modifications were made to this theoretical expression:

1. A constant, **Bk**, was added to account for the background count observed as t --> ∞ ;

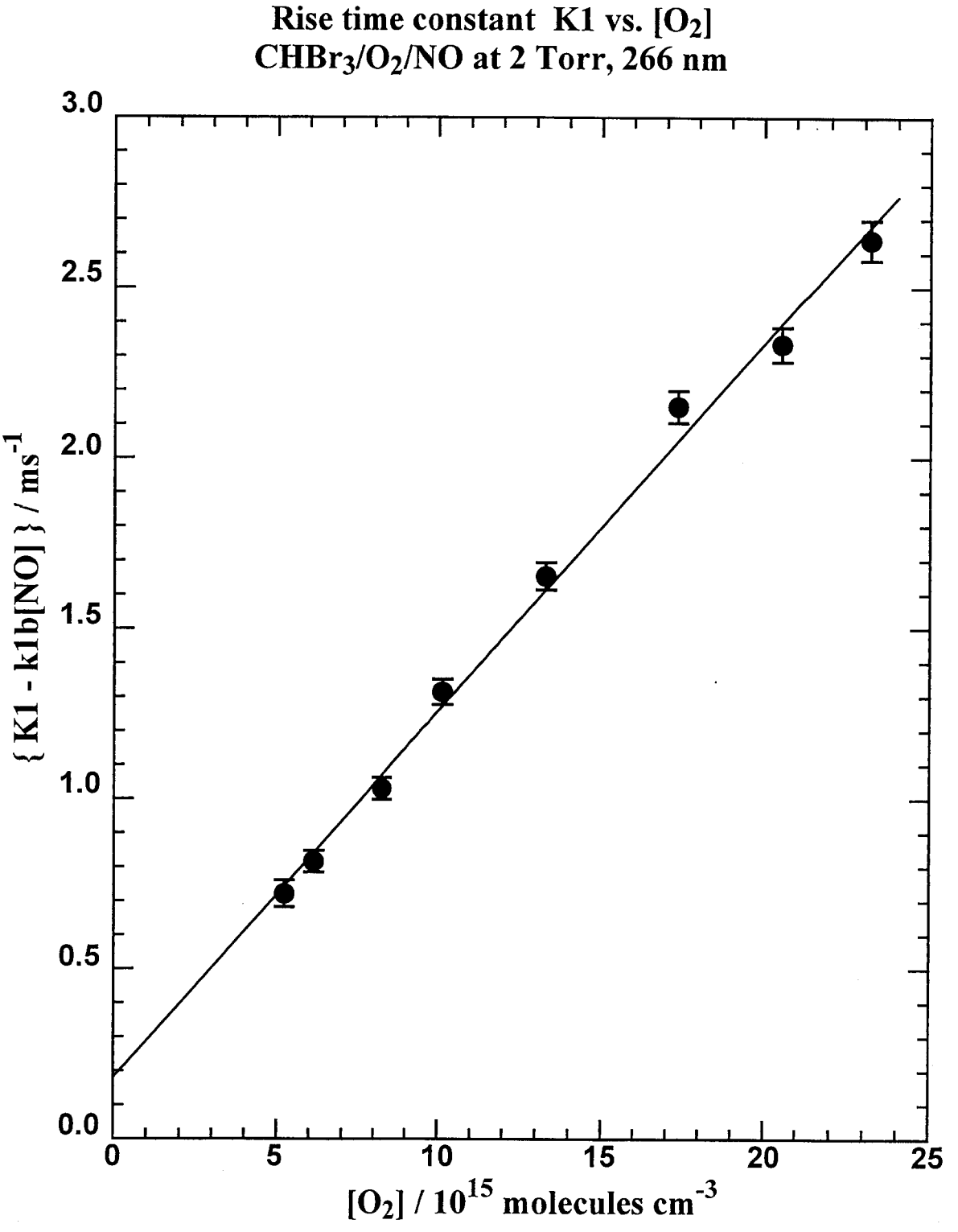
2. A fitted constant, **S1**, is used in place of the term (F1 F2 S0) so that the assumption that every RO decomposes to give a Br atom can be tested by comparing S1/(F1 F2) with S0.

Rise time constant K2 vs. [NO]

$CHBr_3$/air/NO at 10 Torr total pressure
266 nm (17 and 19 June 2002)
303 nm (8 May 2002)



k2a = (1.93 +/- 0.04) 10^{-11} cm^3 $molecule^{-1}$ s^{-1}



Slope = k1a = 1.08 x 10^{-13} cm^3 $molecules^{-1}$ s^{-1}

using k1b = 5.9 x 10^{-13}

Results so far:

P / Torr	k1a / 10^{-13}	k1b / 10^{-13}	k2a / 10^{-11}	S1 / (S0 F1 F2)
10	3.0	~11	1.9	**1.00** ± 0.015 (266 nm) **0.97** ± 0.12 (303 nm)
2	1.1	~6	~2.0	**0.95** ± 0.06 (266 nm)

Conclusion:

The amplitude of the secondary bromine atom signal, S1, when corrected for the intermediate losses of $CHBr_2$ and $CHBr_2O_2$, is the same as the amplitude of the primary bromine atom signal, S0; i.e. all of the $CHBr_2O$ radicals must decompose rapidly to Br + CHBrO (bromoformaldehyde) for the conditions of these experiments.