

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HET\_O\_12

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### HO<sub>2</sub> + aqueous organic aerosol → products

#### Experimental data

substrate	RH / %	Temp./K	p(HO <sub>2</sub> ) / mbar	Reference	Technique/ Comments	
<i>Uptake coefficients: <math>\gamma</math></i>						
< 0.01	levoglucosan	20	296 ± 2	4 × 10 <sup>-9</sup>	Taketani et al., 2010	AFT-LIF (a)
0.01 ± 0.01		40				
0.05 ± 0.01		55				
0.09 ± 0.02		75				
0.13 ± 0.03		92				
0.18 ± 0.07	succinic acid	68	296 ± 2	4 × 10 <sup>-9</sup>	Taketani et al., 2013	AFT-LIF (b)
0.15 ± 0.04	glutaric acid	68				
0.13 ± 0.04	pimelic acid	68				
< 0.004	glutaric acid	32	293 ± 2	4 × 10 <sup>-8</sup>	Lakey et al., 2015	AFT-LIF (c)
0.006 ± 0.002		54				
< 0.004		76				
0.003 ± 0.003	glyoxal	33	293 ± 2	4 × 10 <sup>-8</sup>		
0.008 ± 0.004		80				
< 0.004	malonic acid	55-76	293 ± 2	4 × 10 <sup>-8</sup>		
< 0.004	MEA-H <sub>2</sub> SO <sub>4</sub>	32	293 ± 2	4 × 10 <sup>-8</sup>		
0.005 ± 0.004	MMS	36	293 ± 2	4 × 10 <sup>-8</sup>		
0.007 ± 0.002	Acros HA	32	293 ± 2	4 × 10 <sup>-8</sup>		
0.017 ± 0.003		54				
0.031 ± 0.009		65				
0.06 ± 0.01		76				
0.043 ± 0.009	Leonardite HA	33	293 ± 2	4 × 10 <sup>-8</sup>		
0.07 ± 0.009		51				
0.09 ± 0.009		75				
0.28 ± 0.06	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 10:1 malonic acid /Cu(II)	60	293 ± 2	4 × 10 <sup>-8</sup>	Lakey et al., 2016a	AFT-LIF (d)
0.31 ± 0.08	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 10:1 citric acid /Cu(II)					
0.24 ± 0.05	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 10:1 diaminoethane /Cu(II)					
0.19 ± 0.07	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 10:1 tartronic acid /Cu(II)					
0.003 ± 0.004	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> + 10:1 oxalic acid /Cu(II)					

0.012± 0.007	sucrose / 0.1 M Cu(II)	17	293±2	4×10 <sup>-8</sup>	Lakey et al., 2016b	AFT-LIF (e)
0.021± 0.01		27				
0.073± 0.054		44				
0.044± 0.013		46				
0.15± 0.055		56				
<i>Accommodation</i>						
<i>coefficients: α<sub>b</sub></i>						
0.22± 0.07	sucrose	> 65	293±2	4×10 <sup>-8</sup>	Lakey et al., 2016b	AFT-LIF (e)

### Comments

- (a) Uptake of HO<sub>2</sub> (~10<sup>8</sup> molecule cm<sup>-3</sup>) to levoglucosan particles (mean surface area weighted diameter of around 100 nm, aerosol surface area up to a few 10<sup>-4</sup> cm<sup>2</sup> cm<sup>-3</sup>) at RH between 20 and 92 %. HO<sub>2</sub> was generated by the photolysis of H<sub>2</sub>O in air and detected as OH (by LIF) following conversion in reaction with NO.
- (b) Setup and conditions as in (a); uptake to dicarboxylic acid particles (mean surface area weighted diameter of 110-200 nm, aerosol surface area up to a few 10<sup>-4</sup> cm<sup>2</sup> cm<sup>-3</sup>) was measured at RH = 28 and 68 %; only values at 68% are listed in the table, since at 29%, the particles were effloresced. The study also included adipic acid, which was assumed solid at both RH conditions and thus not included in the table. Uptake coefficients on the solid particles were 0.07, 0.07, 0.02 and 0.06 for succinic, glutaric, adipic and pimelic acids, respectively, at 28% RH, and 0.06 for adipic acid at 68% RH.
- (c) Uptake of HO<sub>2</sub> (~ 10<sup>9</sup> molecule cm<sup>-3</sup>) to aqueous organic particles (peak surface area weighted diameter of 60-90 nm) at RH between 30 and 80 %. HO<sub>2</sub> was generated by the photolysis of H<sub>2</sub>O in N<sub>2</sub> or air and detected as OH (by LIF) following conversion in reaction with NO. The solutions mono ethanol amine sulfate-H<sub>2</sub>SO<sub>4</sub> (MEA-H<sub>2</sub>SO<sub>4</sub>) and monomethyl amine sulfate (MMS) were adjusted to a pH of 8.1 and 8.5 respectively, by adding H<sub>2</sub>SO<sub>4</sub> to the corresponding amine solutions. The Acros humic acid (HA) aerosol had estimated Cu and Fe contents of 5.5×10<sup>-4</sup> M and 8.3×10<sup>-2</sup> M, respectively, while for Leonardite humic acid these were 1.2×10<sup>-4</sup> M and 4.8×10<sup>-3</sup> M, respectively. In the other solutions, Fe and Cu contents were estimated at 10<sup>-5</sup> – 10<sup>-3</sup> for Fe and 10<sup>-7</sup> – 10<sup>-5</sup> for Cu. Uptake coefficients were determined from measuring the first order loss rate coefficient of HO<sub>2</sub> along the flow tube as a function of aerosol surface area varied between 0 and 10<sup>-3</sup> cm<sup>2</sup> cm<sup>-3</sup>.
- (d) Setup as in (c). Mixed (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> / CuSO<sub>4</sub> aerosol (0.3 M Cu(II) at 60 % RH) with the various organics added at organic:Cu ratio between 1:1 and 10:1 (only values for 10:1 shown in the table). Effect of complexing agent investigated in more detail for EDTA, where at EDTA:Cu = 1:1 the uptake coefficient was 0.009± 0.009, while for EDTA:Cu = 6:5, γ = 0.005 ± 0.005
- (e) Setup as in (c), with slightly different configuration for gas flows (AFT operated below ambient pressure, at 915 mbar). The particles contained CuSO<sub>4</sub> (~0.1 M) as a scavenger for HO<sub>2</sub>. Detailed depth resolved model calculations with KM-SUB indicated that uptake was limited by accommodation at RH above 65 %, justifying listing the average uptake coefficient as α<sub>b</sub> in the table. Measurements at lower RH were driven by reaction and diffusion in the bulk, and by a surface process.

### Preferred Values

Parameter	Value	T/K
α <sub>b</sub>	> 0.2	290 - 300
γ	0.005	290 - 300
k <sub>TMI</sub> (M <sup>-1</sup> s <sup>-1</sup> )	5 × 10 <sup>5</sup>	290 - 300
k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )	2.4×10 <sup>9</sup> exp(-2360/T)	290 - 300
k <sub>3</sub> (M <sup>-1</sup> s <sup>-1</sup> )	1.6×10 <sup>10</sup> exp(-1510/T)	290 - 300

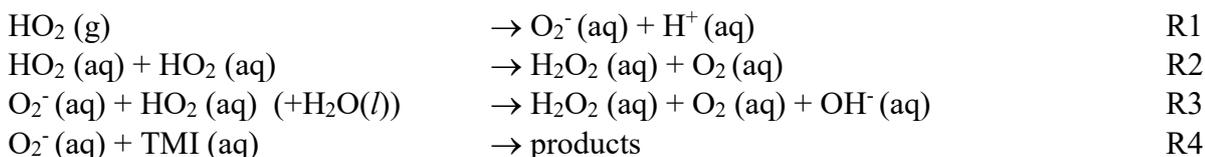
<i>uncertainty</i>		
$\Delta \log(k_{\text{TMI}})$	1	290 – 300
$\Delta \log(k_{2,3})$	0.3	290 – 300

### Comments on Preferred Values

In the presence of Cu(II) at concentrations above 0.01 M, the HO<sub>2</sub> uptake into concentrated aqueous aerosol solutions with organic solutes is limited by bulk accommodation as confirmed by the dataset by Lakey et al. (2016b) for sucrose aerosol at high RH. The measured value of  $\alpha_b$  is similar to that reported by the same group for other aqueous solutions, e.g., (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. This is at the lower end of values reported by other groups for other solutions. We recommend the same lower limit to  $\alpha_b$  for consistency among the aqueous solution datasheets for HO<sub>2</sub>.

In the absence of transition metals, HO<sub>2</sub> uptake coefficients are within the range observed for inorganic aqueous solutions. As with the inorganic salt aerosol, uptake to dry (effloresced) particles is by a factor of 5 to 10 smaller than on the corresponding aqueous particles and comparable to other, non-soluble organics or soot (Lakey et al., 2015; Taketani et al., 2010; Bedjanian et al., 2005). The large discrepancy in absolute uptake coefficient values between the Taketani et al. and Lakey et al. studies remains unresolved. Possible reasons include different flow tube residence times and surface to volume ratios, and possible contamination by transition metals. The presence of transition metal ions contamination was carefully checked in the Lakey et al. (2015) study, and is the cause of the higher uptake coefficients observed on humic acid aerosol.

The uptake of HO<sub>2</sub> in aqueous solution is presently believed to be driven by self-reaction and acid-base dissociation of HO<sub>2</sub> (pKa ~ 4.7) with formation of H<sub>2</sub>O<sub>2</sub> (R2, R3). In the presence of transition metal ions (TMI) the reaction of HO<sub>2</sub> and especially O<sub>2</sub><sup>-</sup> (R4) can be important:



If a first-order loss process for HO<sub>2</sub> or O<sub>2</sub><sup>-</sup> in the aqueous phase dominates (e.g. reaction with TMI such as Cu(II)), the uptake coefficient can be calculated from the expression below:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{TMI}}}$$

$$\frac{1}{\Gamma_{\text{TMI}}} = \frac{c}{4H^{\text{eff}} RT \sqrt{D_1 k_{\text{TMI}} [\text{TMI}] [\coth(r_p / l_{\text{rd}}) - (l_{\text{rd}} / r_p)]}} \quad l_{\text{rd}} = \sqrt{\frac{D_1}{k_{\text{TMI}} [\text{TMI}]}} \quad (1)$$

$$H^{\text{eff}} = H^{\text{HO}_2} (1 + K_{\text{eq}} / [\text{H}^+])$$

$$K_{\text{eq}} = 2.1 \times 10^{-5} \text{ M at 298 K (Jacob, 2000)}$$

$$H^{\text{HO}_2} = 9.5 \times 10^{-6} \exp(5910/T) \text{ M atm}^{-1} \text{ (Hanson et al., 1992)}$$

$k_{\text{TMI}}$  is the second order rate coefficient for the reaction of HO<sub>2</sub> and O<sub>2</sub><sup>-</sup> with transition metal ions; the preferred value is justified in the datasheet VI.A3.10. For low viscosity aqueous solutions, the diffusivity of HO<sub>2</sub> can be approximated by that in pure water (Schwartz, 1984; Thornton et al., 2008):

$$D_1 = \{1 \times 10^{-5} (T/298)\} / (1.09 \times 10^8 \exp(-0.068T) + 0.873) \text{ cm}^2 \text{ s}^{-1}$$

where the denominator was derived from a fit to the water viscosity data of Hallett (1963).  $D_1$  needs to be assessed individually in presence of organic solutes that lead to strong changes to viscosity. The size dependent correction factor, with  $r_p$  denoting the particle radius and  $l_{\text{rd}}$  the reacto-diffusive length, assures proper representation when the kinetic regime changes from

reaction-diffusion towards volume limited kinetics at low TMI concentrations, low diffusivity and / or small particle sizes.

Figure 1 shows that Equation (1) fairly well reproduces the data by Lakey et al. (2016b) of HO<sub>2</sub> uptake to Cu(II) doped sucrose aerosol as a function of RH, for two different estimates of  $D_1$  of HO<sub>2</sub> in sucrose solution based on the diffusivity of H<sub>2</sub>O reported by Zobrist et al. (2011) or by Price et al. (2014). Lakey et al. (2016b) use a depth resolved model to argue that due to the increasing viscosity and thus decreasing diffusivity the kinetic regime transits from accommodation limitation into diffusion limitation at intermediate RH, while at low RH, the authors suggest that a surface process limits uptake when slow diffusion in the bulk becomes unimportant. We prefer using Equation (1) with sufficient error bounds to reflect the uncertainty of the contribution of a surface process at low RH and the uncertainty related to the diffusivity at low RH.

Apart from affecting viscosity and thus diffusivity, many organic solutes are chelating agents for Cu(II) and thus may potentially reduce its reactivity as demonstrated for EDTA and oxalic acid by Lakey et al. (2016a). However, as the authors caution, metal oxalate (and other) complexes may also have an impact on viscosity, surface tension and hygroscopic properties, all of which may also influence HO<sub>2</sub> uptake.

In the absence of TMI, the rates of loss of aqueous-phase HO<sub>2</sub> are quadratically dependent on [HO<sub>2</sub>]<sub>aq</sub> and [O<sub>2</sub><sup>-</sup>]<sub>aq</sub>. The uptake coefficient is thus strongly dependent on the gas-phase concentration of HO<sub>2</sub> and becomes small at low, relevant HO<sub>2</sub> concentrations. Thornton and Abbatt (2005) suggest that the rate of loss of HO<sub>2</sub> from the gas-phase (in molecule cm<sup>-3</sup> s<sup>-1</sup>) is best described by a system in thermodynamic (Henry's law) equilibrium so that (Thornton et al., 2008):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{self}}} \quad \frac{1}{\Gamma_{\text{self}}} = \frac{3cN_{\text{Av}}}{8000(H^{\text{eff}} RT)k_{\text{aq}}[\text{HO}_2]_p} \quad (2)$$

$k_{\text{aq}}$  can be calculated from the rate coefficients for R2 ( $k_2$ ) and R3 ( $k_3$ ) (Bielski et al., 1985) and the pH:

$$k_{\text{aq}} = \frac{k_2 + \left( \frac{K_{\text{eq}}}{[\text{H}^+]_{\text{aq}}} \right) k_3}{\left( 1 + \frac{K_{\text{eq}}}{[\text{H}^+]_{\text{aq}}} \right)^2}$$

At low concentrations of HO<sub>2</sub> (whereby the self-reaction and reaction with O<sub>2</sub><sup>-</sup> are inefficient), values of  $\gamma$  of < 0.005 are calculated, which are somewhat below the values reported by Lakey et al. (2015), but much lower than the uptake coefficients for levoglucosan or dicarboxylic acids reported by Taketani et al. (2010, 2013), as discussed above (Figure 2). As discussed by Hanson et al. (1992) and Thornton and Abbatt (2005), the parameterization suggested here is very sensitive to the solubility of HO<sub>2</sub> ( $H^{\text{HO}_2}$ ), its temperature dependence and on the aerosol pH (Figure 3). While for glutaric acid, aerosol pH as returned by the E-AIM model (Clegg et al., 2006) is about 1, buffering by contaminants (NH<sub>3</sub>, CO<sub>2</sub>) may lead to higher aerosol pH in an experiment. Therefore, in Figure 2, the uptake coefficient is calculated for pH 1 and 4 for comparison.

The above schemes do not account for the RH dependence of uptake observed by Taketani et al. (2010) for levoglucosan. Since the size change cannot account for the relative increase of the reported uptake coefficient, a strong salting-out effect would have to be invoked. A significant RH dependence is not observed by Lakey et al. (2016) for the dicarboxylic acids or glyoxal. According to the above parameterisation, it seems rather that the small increase in size and related increase in the uptake coefficient may be counteracted by the increase in pH due to dilution towards higher RH.

Since the studies of Lakey et al on ammonium sulfate (without and with variable amounts of Cu(II)) are consistent with the parameterization given above and are also in line with the measurement by Thornton and Abbatt (2005) at higher HO<sub>2</sub> concentration (datasheet VI.A3.10), we base our recommendation on the their datasets. The preferred temperature and humidity independent single value for the uptake coefficient is an average of the uptake coefficients reported for organic solutes (except those for which an upper limit has been reported and except those for humic acids, which are affected by Cu).

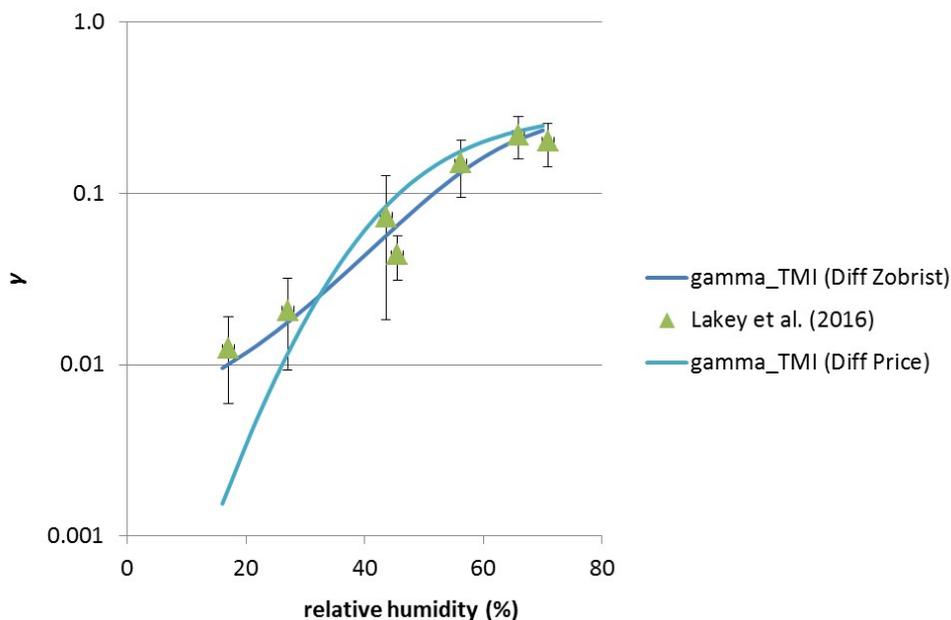
If more information about aerosol pH and viscosity is available, we suggest using Equations (1) and (2) to consistently describe uptake of HO<sub>2</sub> in presence and absence of transition metal ions. At low HO<sub>2</sub> concentrations, the overall  $\gamma$  can be obtained by adding the corresponding resistors:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{TMI}} + \Gamma_{\text{self}}} \quad (4)$$

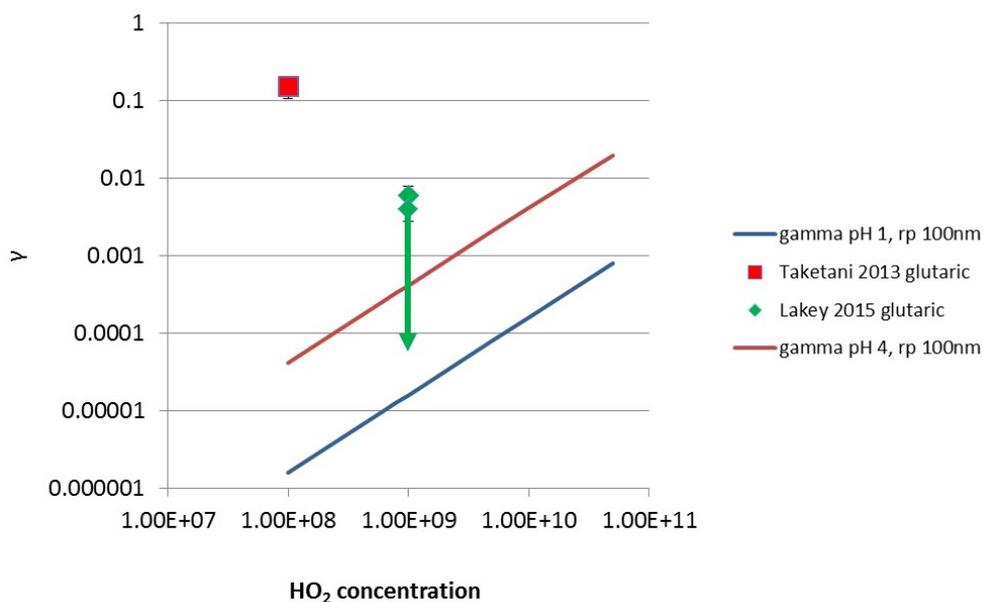
We refer to recent publications for a more detailed description of the effect of different parameterisation schemes (Thornton et al., 2008; Macintyre and Evans, 2011; Mao et al., 2013).

## References

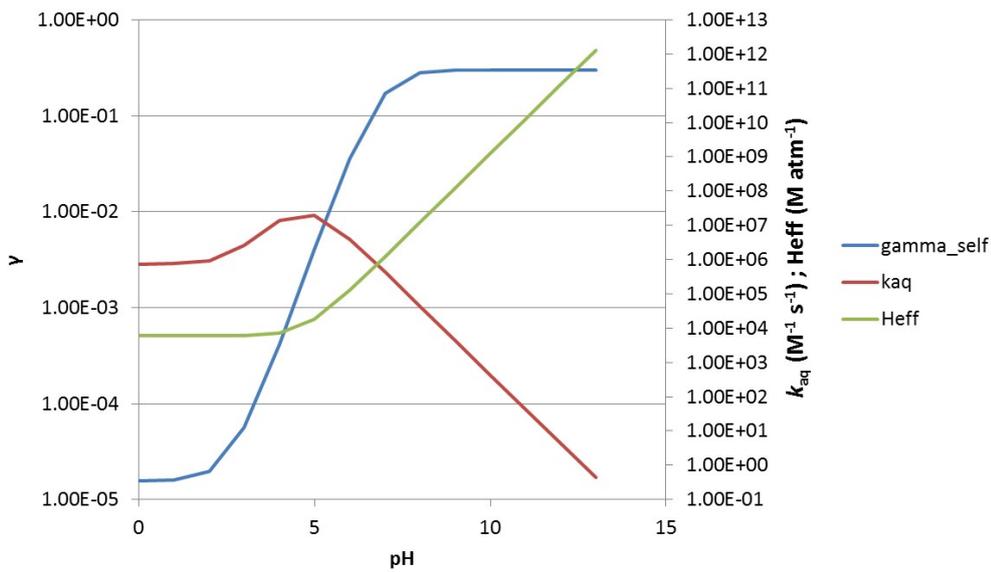
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**Figure 1:** Uptake coefficient of HO<sub>2</sub> on sucrose aerosol as a function of RH at 292 K. Symbols: data by Lakey et al. (2016); lines:  $\gamma$  based on Equation (1) for 100 nm particle radius, pH 4.1, with  $D_1$  estimated for pure sucrose based on  $D_1$  of H<sub>2</sub>O in sucrose by Zobrist et al. (2011) (dark blue) or Price et al. (2014) (light blue).



**Figure 2:** Uptake coefficient of HO<sub>2</sub> on glutaric acid aerosol as a function of HO<sub>2</sub> concentration at 292 K. Symbols: data by Lakey et al. (2016) and Taketani et al. (2013), with the upper end of the green arrow indicating the upper limit for part of the data points; lines:  $\gamma$  based on Equation (2) for 100 nm particle radius, pH 1 (blue) and pH 4 (red), with  $D_1$  equivalent to that for pure water given above.



**Figure 3:** Uptake coefficient of HO<sub>2</sub> on aqueous solution as a function of pH at 292 K. Blue line (left y-axis):  $\gamma$  based on Equation (2) for 100 nm particle radius, HO<sub>2</sub> concentration of  $10^9$  molecule  $cm^{-3}$ , with  $D_1$  equivalent to that for pure water given above; green line (right y-axis): effective Henry's law constant; red line (right y-axis):