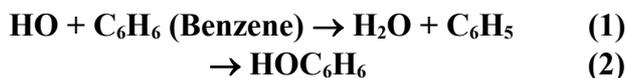


# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO<sub>x</sub>\_AROM1

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated August 2008; last change in preferred values August 2008.



## Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.59 \pm 0.12) \times 10^{-12}$	298	Davis et al., 1975	FP-RF (a)
$(1.24 \pm 0.12) \times 10^{-12}$	298	Hansen et al., 1975	FP-RF (b)
$(1.20 \pm 0.15) \times 10^{-12}$	297.6	Perry et al., 1977	FP-RF (c)
$(1.32 \pm 0.30) \times 10^{-12}$	304.4		
$(1.33 \pm 0.25) \times 10^{-12}$	305.8		
$(1.66 \pm 0.25) \times 10^{-12}$	322.7		
$(2.6 \pm 1.5) \times 10^{-13}$	396.2		
$(3.4 \pm 0.7) \times 10^{-13}$	396.4		
$(3.4 \pm 1.2) \times 10^{-13}$	405.8		
$(4.5 \pm 0.7) \times 10^{-13}$	422.0		
$3.1 \times 10^{-13} \exp[-(270 \pm 220)/T]$	250-298	Tully et al., 1981	FP-RF (d)
$(1.04 \pm 0.08) \times 10^{-12}$	250		
$(1.20 \pm 0.09) \times 10^{-12}$	270		
$(1.24 \pm 0.09) \times 10^{-12}$	298		
$(5.43 \pm 0.23) \times 10^{-13}$	542		
$(6.39 \pm 0.29) \times 10^{-13}$	621		
$(6.82 \pm 0.74) \times 10^{-13}$	630		
$(6.06 \pm 0.34) \times 10^{-13}$	653		
$(1.02 \pm 0.04) \times 10^{-12}$	715		
$(1.20 \pm 0.16) \times 10^{-12}$	742		
$(1.59 \pm 0.09) \times 10^{-12}$	817		
$(1.90 \pm 0.20) \times 10^{-12}$	895		
$(2.26 \pm 0.13) \times 10^{-12}$	917		
$(2.35 \pm 0.23) \times 10^{-12}$	981		
$(2.20 \pm 0.34) \times 10^{-12}$	1017		
$(7.6 \pm 1.5) \times 10^{-13}$	244	Lorenz and Zellner, 1983	PLP-RF (e)
$(1.15 \pm 0.25) \times 10^{-12}$	298 ± 2		
$(1.26 \pm 0.25) \times 10^{-12}$	336		
$(8.3 \pm 1.7) \times 10^{-13}$	373		
$(5.0 \pm 1.0) \times 10^{-13}$	384		
$(4.0 \pm 0.9) \times 10^{-13}$	453		
$(4.3 \pm 0.9) \times 10^{-13}$	523		
$(8.8 \pm 0.4) \times 10^{-13}$	295	Wahner and Zetzsch, 1983	FP-RF (f)
$(1.02 \pm 0.2) \times 10^{-12}$	296	Rinke and Zetzsch, 1984	FP-RF (f)
$3.5 \times 10^{-11} \exp[-(2300 \pm 100)/T]$	787-1409	Madronich and Felder, 1985	FP-RF
$2.3 \times 10^{-12} \exp[-(190 \pm 60)/T]$	239-354	Witte et al., 1986	FP-RF (g)
$(1.05 \pm 0.05) \times 10^{-12}$	299		

$(1.40 \pm 0.23) \times 10^{-12}$	234	Wallington et al., 1987	PF-RF (h)
$(1.30 \pm 0.19) \times 10^{-12}$	263		
$(1.29 \pm 0.14) \times 10^{-12}$	296		
$(1.93 \pm 0.37) \times 10^{-13}$	393		
$(2.58 \pm 0.34) \times 10^{-13}$	438		
$k_1 = (4.6 \pm 2.8) \times 10^{-14}$	298	Knispel et al., 1990	FP-RF (i)
$k_2 = (1.06 \pm 0.09) \times 10^{-12}$	298		
$k_1 = (1.9 \pm 1.2) \times 10^{-14}$	315		
$k_2 = (1.02 \pm 0.03) \times 10^{-12}$	315		
$k_1 = (1.2 \pm 0.6) \times 10^{-14}$	333		
$k_2 = (1.05 \pm 0.12) \times 10^{-12}$	333		
$k_1 = (2.1 \pm 0.9) \times 10^{-14}$	354		
$k_2 = (8.8 \pm 2.3) \times 10^{-13}$	354		
$2.0 \times 10^{-14} \exp[(1420 \pm 250)/T]$	345-385	Lin et al., 1994	PLP-LIF (j)
$(1.09 \pm 0.04) \times 10^{-12}$	345-361		
$(1.2 \pm 0.2) \times 10^{-12}$	298	Bjergbakke et al., 1996	PR-UVA (k)
$(1.10 \pm 0.07) \times 10^{-12}$	297 ± 2	Bohn and Zetzsch, 1999	PLP-UVA (l)
$(1.06 \pm 0.07) \times 10^{-12}$	297 ± 2		
$8.0 \times 10^{-11} \exp[-(3199 \pm 241)/T]$	908-1736	Seta et al., 2006	SH-LIF (m)
<i>Relative Rate Coefficients</i>			
$\leq 2.4 \times 10^{-12}$	304 ± 1	Doyle et al., 1975	RR (n)
$8.4 \times 10^{-13}$	300	Cox et al., 1980	RR (o)
$9.3 \times 10^{-13}$	300	Barnes et al., 1982	RR (p)
$(1.35 \pm 0.06) \times 10^{-12}$	~298	Ohta and Ohyama, 1985	RR (q)
$(1.19 \pm 0.44) \times 10^{-12}$	296 ± 1	Edney et al., 1986	RR (r)
$(1.19 \pm 0.47) \times 10^{-12}$	297 ± 2	Sommerlade et al., 1993	RR (s)
$2.93 \times 10^{-12} \exp[-(288.3 \pm 84.8)/T]$	274-363	Semadeni et al., 1995	RR (t)
$(1.12 \pm 0.06) \times 10^{-12}$	299		

### Comments

- (a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.
- (b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 50-600 Torr (67-800 mbar).
- (c) Non-exponential HO radical decays were observed at temperatures between 331 K and 381 K. Rate coefficients were measured at 100 Torr (133 mbar) of Ar diluent.
- (d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 25-100 Torr (33-133 mbar) of He, 50-200 Torr (67-267 mbar) of Ar, and at 100 Torr (133 mbar) of SF<sub>6</sub>, with no significant pressure dependence being observed over these ranges. Non-exponential HO radical decays were observed at temperatures between 320 K and 400 K.
- (e) At 298 ± 2 K, rate coefficients were measured over the pressure range 1.5-112 mbar (1.1-84 Torr) of Ar diluent. The rate coefficients increased with increasing pressure up to ~40 mbar (30 Torr), with no observed effect of pressure above 40 mbar.
- (f) Rate coefficients were measured over the pressure ranges 67-173 mbar (50-130 Torr) of Ar diluent (Wahner and Zetzsch, 1983) and 33-666 mbar (25-500 Torr) of He diluent (Rinke and Zetzsch, 1984), with a slight decrease in rate coefficient being observed below 133 mbar (100 Torr) pressure in both cases. The cited rate coefficients are at 133 mbar pressure.
- (g) Rate coefficients were measured at 133 and/or 200 mbar pressure of Ar diluent (the 299 K rate coefficient cited in the table is at 133 mbar pressure). At 294 K, rate coefficients were also

measured over the pressure range 1.3-533 mbar (1.0-400 Torr) of Ar diluent, with a decrease in rate coefficient being observed below ~67 mbar (50 Torr) pressure.

- (h) No effect of pressure was observed over the range 25-50 Torr (33-67 mbar) of Ar diluent. Non-exponential HO radical decays were observed at 353 K.
- (i) Rate coefficients  $k_1$  and  $k_2$  were derived from fitting the observed non-exponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression  $k_1 = C T^2 \exp(-D/T)$ , a global fit to the experimental data resulted in rate coefficients  $k_1$  of  $6.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K,  $1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 315 K,  $1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 333 K and  $2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 354 K.
- (j) Rate coefficients  $k$  were derived from fitting the observed non-exponential HO radical decays, measured over time periods at total pressures of 250-500 Torr (333-667 mbar) of He, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. The cited Arrhenius expression over the temperature range 345-385 K was obtained assuming that  $k_1 = 0$ .
- (k)  $k$  was determined from the decay rates of HO radicals monitored by absorption at 309 nm.
- (l) Experiments were carried out in  $\text{N}_2$  and  $\text{O}_2$  diluent at total pressures of 0.101-1.00 bar (75-750 Torr) of  $\text{N}_2$  and 0.973-0.980 bar (730-735 Torr) of  $\text{O}_2$ , with measured rate coefficients of  $(1.10 \pm 0.07) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in  $\text{N}_2$  and  $(1.06 \pm 0.07) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in  $\text{O}_2$ .
- (m) HO radicals were generated by shock heating of nitric acid or *tert*-butyl hydroperoxide.
- (n) HO radicals generated by the photolysis of organic- $\text{NO}_x$  mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of benzene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + n\text{-butane}) \leq 1$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + n\text{-butane}) = 2.41 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 304 K (IUPAC, current recommendation).
- (o) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + \text{ethene})$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- (p) HO radicals were generated by dark decomposition of  $\text{HOONO}_2$  in the presence of NO at atmospheric pressure of  $\text{N}_2$  or air. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + \text{ethene}) = 0.11$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- (q) HO radicals generated by the photolysis of  $\text{H}_2\text{O}_2$  at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Benzene and *n*-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + n\text{-hexane}) = 0.26 \pm 0.01$  is placed on an absolute basis using a 298 K rate coefficient of  $k(\text{HO} + n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson and Arey, 2003).
- (r) HO radicals generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air at 1 bar pressure. Benzene and propane (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + \text{propane})$  is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + \text{propane}) = 1.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (IUPAC, current recommendation).
- (s) HO radicals generated by the photolysis of  $\text{NO}_x$  in the presence of organics in air at 70 Torr (93 mbar) pressure. Benzene and *n*-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + n\text{-hexane})$  is placed on an absolute basis

using a rate coefficient of  $k(\text{HO} + n\text{-hexane}) = 5.17 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K (Atkinson and Arey, 2003).

- (t) HO radicals generated by the photolysis of  $\text{CH}_3\text{ONO}$  in air at atmospheric pressure. Benzene and toluene (the reference compound) were monitored by GC, and the measured rate coefficient ratio  $k(\text{HO} + \text{benzene})/k(\text{HO} + \text{toluene}) = 1.625 \exp[-(628.3 \pm 84.8)/T]$  over the temperature range 274-363 K is placed on an absolute basis using a rate coefficient of  $k(\text{HO} + \text{toluene}) = 1.8 \times 10^{-12} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation).

### Preferred Values

$k = 2.3 \times 10^{-12} \exp(-190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 230-350 K.

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k_1 = 3.8 \times 10^{-11} \exp(-2520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 330-1410 K.

$k_1 = 8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

### Reliability

$\Delta \log k = \pm 0.10$  at 298 K.

$\Delta(E/R) = \pm 200$  K.

$\Delta \log k_1 = \pm 0.5$  at 298 K.

$\Delta(E_1/R) = \pm 300$  K.

### Comments on Preferred Values

Absolute rate studies show that the reaction of HO radicals with benzene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-benzene adduct,  $\text{HOC}_6\text{H}_6$ , being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <50-100 Torr, channel (2) is in the fall-off regime at room temperature (Davis et al., 1975; Lorenz and Zellner, 1983; Wahner and Zetzsch, 1983; Rinke and Zetzsch, 1984; Witte and Zetzsch, 1986; Baulch et al., 1988; Goumri et al., 1991), with a limiting low-pressure rate coefficient at  $297 \pm 3$  K of  $k_0(\text{He}) = 1.7 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  (Goumri et al., 1991). At temperatures >450 K, decomposition of the HO-benzene adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-benzene adduct is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are generally observed.

The >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985), which are attributed to those for pathway (1), and the values of  $k_1$  derived by Knispel et al. (1990) from HO radical decay curves at 298-354 K indicate that an Arrhenius fit is adequate. The preferred values of  $k_1$  are obtained from a least-squares fit of the >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985) and the rate coefficients  $k_1$  of Knispel et al. (1990) at 333 K and 354 K (their rate coefficients  $k_1$  at 298 K and 315 K have high associated uncertainties and are significantly higher than the rate coefficients  $k_1$  derived by Knispel et al. (1990) from a global fit (see Comment (i)), and are therefore not used in the evaluation of  $k_1$ ). The shock tube data of Seta et al. (2006) at 908-1736 K are in excellent agreement with this preferred expression for  $k_1$ .

The preferred values of  $k$  at  $\leq 350$  K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Lorenz and Zellner (1983), Witte et al. (1985) [which are judged to supersede the earlier room temperature studies of Wahner and Zetzsch (1983) and Rinke and Zetzsch (1984)], Wallington et al. (1987), Knispel et al. (1990) and Bohn and Zetzsch (1999). The rate

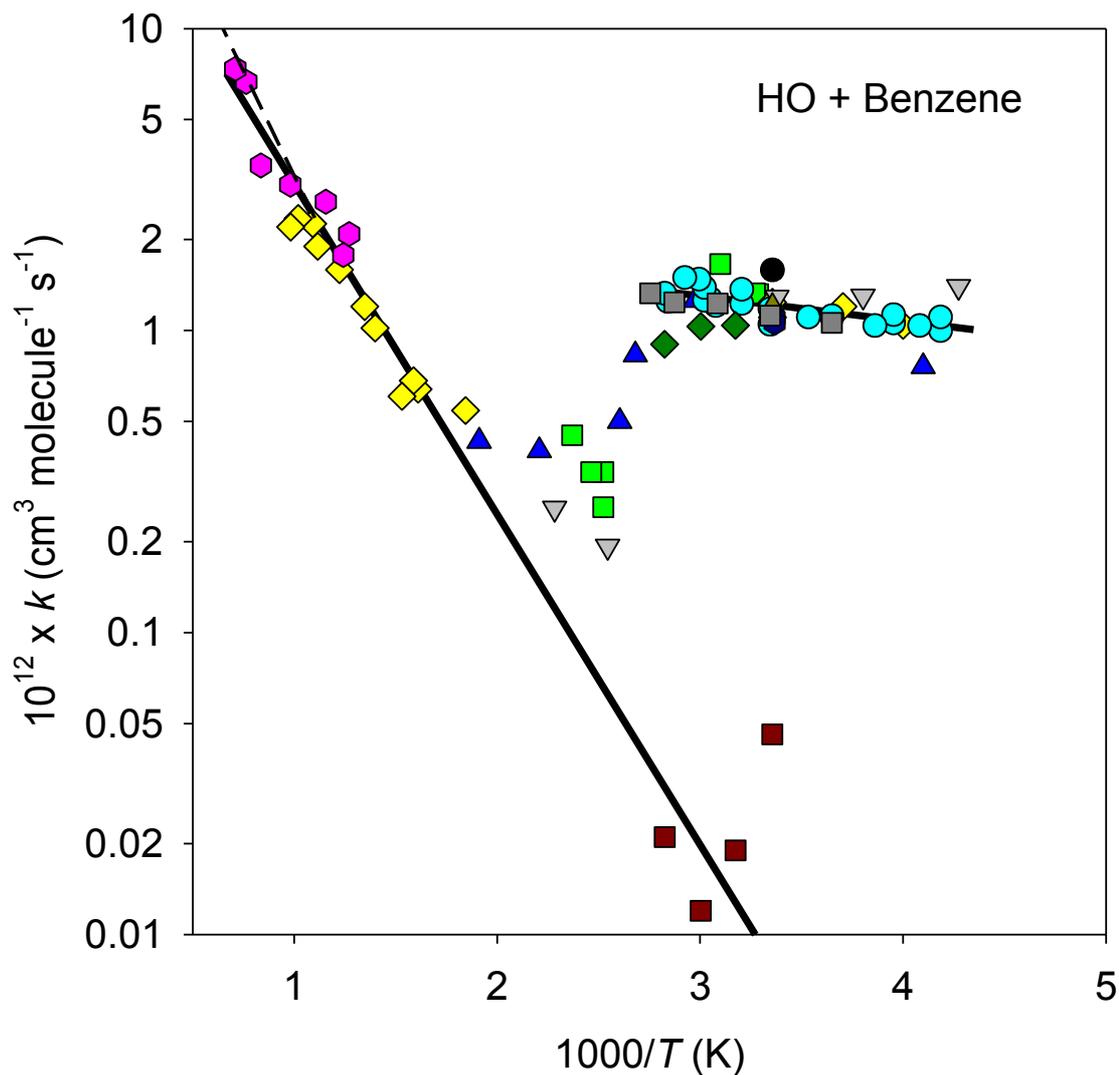
coefficients at  $\leq 350$  K of Cox et al. (1981), Barnes et al. (1982), Wahner and Zetzsch (1983), Rinke and Zetzsch (1984), Ohta and Ohyama et al. (1985), Edney et al. (1986), Somerlade et al. (1993), Lin et al. (1994), Semadeni et al. (1995) and Bjergbakke et al. (1996) are in good agreement with the preferred  $\leq 350$  K rate expression. While the rate coefficients derived by Lin et al. (1994) from non-exponential HO radical decays over the restricted temperature range 345-385 K show a negative temperature dependence, this arises from the rate coefficients at  $\geq 367$  K and may be due to fall-off effects; their rate coefficients at 345-361 K are independent of temperature and  $\sim 20\%$  lower than the preferred values. Particularly noteworthy is that the rate coefficients of Semadeni et al. (1995) measured relative to those for toluene are in excellent agreement with the preferred expression, indicating that the preferred values for HO + benzene and HO + toluene (IUPAC, current recommendation) are internally self-consistent.

At atmospherically-relevant temperatures, the reaction proceeds essentially totally by channel (2), with channel (1) accounting for  $< 2\%$  of the overall reaction at 298 K and even less at lower temperatures.

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- Recommendations
- Davis et al. (1975)
- ▼ Hansen et al. (1975)
- Perry et al. (1977)
- ◆ Tully et al. (1981)
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- ◆ Madronich and Felder (1985)
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- ▽ Wallington et al. (1987)
- Knispel et al. (1990),  $k_1$
- ◆ Knispel et al. (1990)
- ▲ Bjergbakke et al. (1996)
- ◆ Bohn and Zetzsch (1999)
- Barnes et al. (1982)
- ▼ Ohta and Ohyama (1985)
- Semadeni et al. (1995)
- - - Seta et al. (2006)



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