



Temperature dependence of the rate coefficients of the OH-initiated oxidation of trimethylphenols between 283 and 313 K

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INTRODUCTION

Aromatic hydrocarbons (AH), such as benzene, toluene, and the isomers of xylene and trimethylbenzene are emitted to the atmosphere mainly by anthropogenic activities as primary pollutants. The high reactivity of aromatics toward hydroxyl radicals (OH) results in an appreciable contribution to photooxidant and SOA formation in urban areas. AH are also associated with human health problems (Calvert et al., 2003). The OH radical initiated oxidation of benzene, toluene, xylene and trimethylbenzene produces phenol, cresols, dimethylphenols and trimethylphenols, respectively (Smith et al., 1999). Trimethylphenols are used widely in chemical industry and are found in fossil fuels, the aqueous environment, tobacco smoke, etc. Trimethylphenols possess carcinogenic and phytotoxic properties. The aim of this study was to determine rate coefficients for the reaction of trimethylphenol isomers with OH radicals in order to assess the relative importance of these reactions as atmospheric loss processes. Presented here are determinations of rate coefficients for the reactions of OH radicals with four trimethylphenol isomers as a function of temperature using a relative kinetic technique. To our knowledge no other temperature dependent studies of the rate coefficients for these reactions are available in the literature.

RESULTS

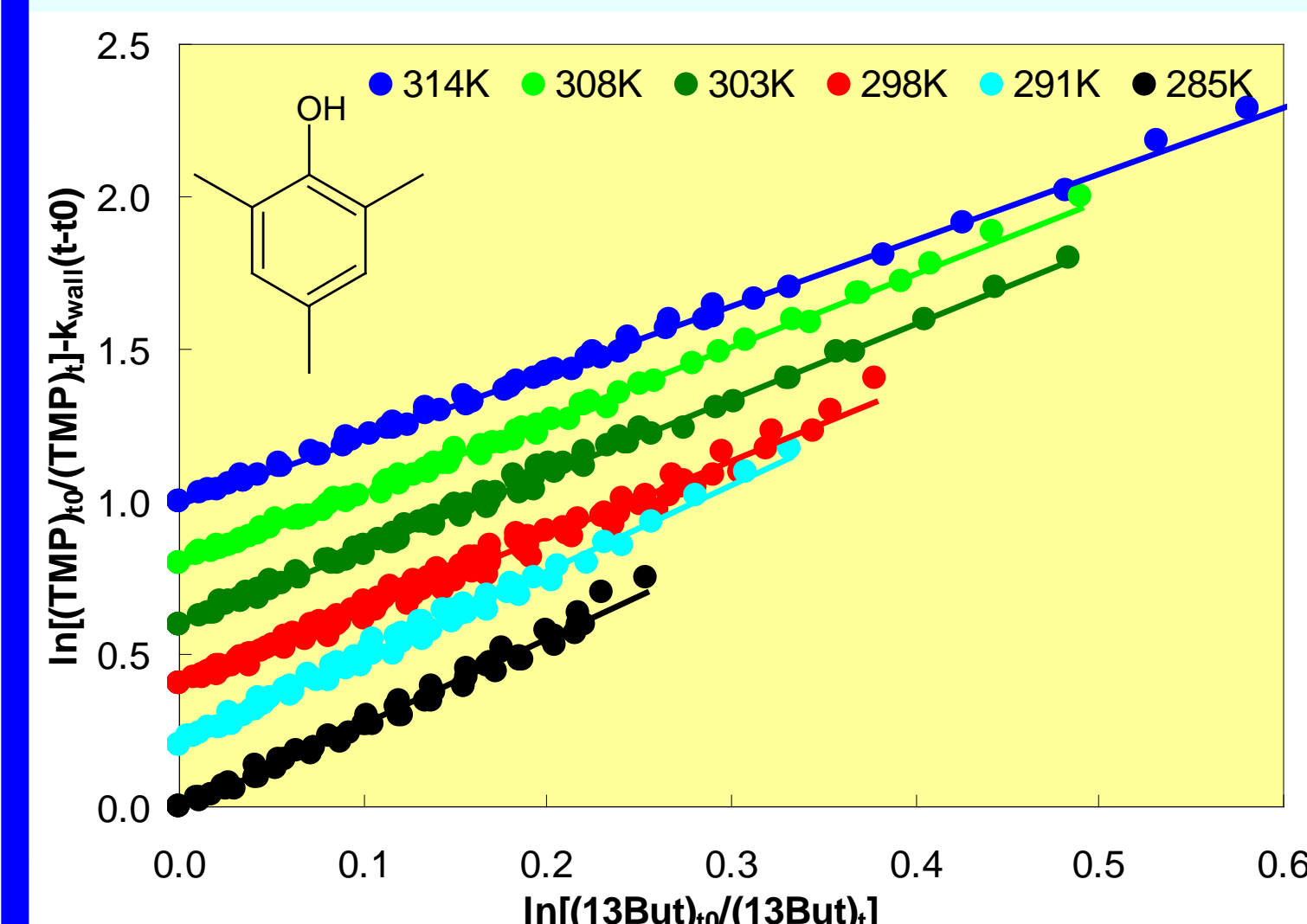


Fig. 1. Kinetic data plotted according to eq (1) for the reaction of OH radicals with 236TMP at different temperatures using 1,3-butadiene as reference hydrocarbon. The data have been displaced vertically for clarity.

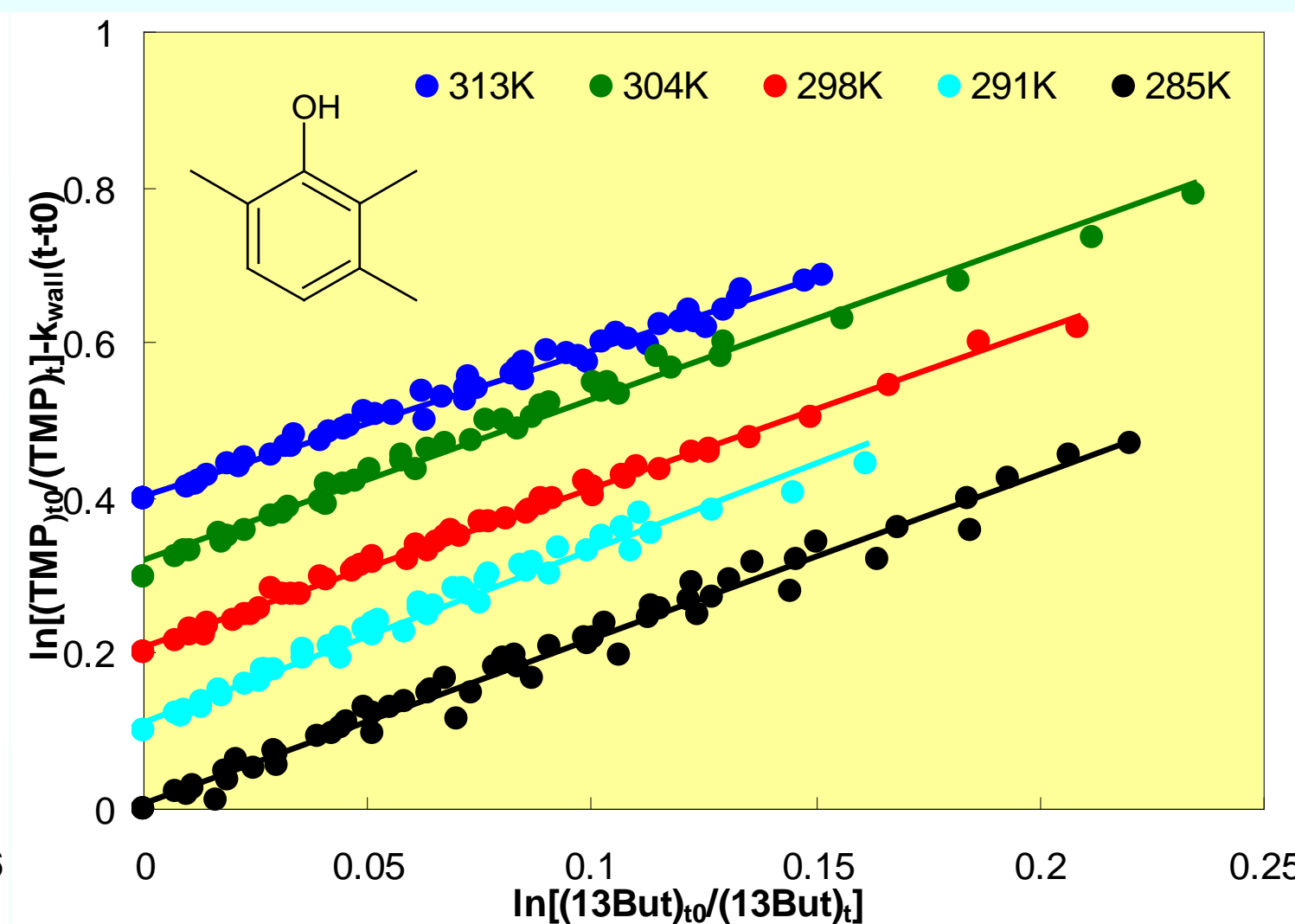


Fig. 2. Kinetic data plotted according to eq (1) for the reaction of OH radicals with 245TMP at different temperatures using 1,3-butadiene as reference hydrocarbon. The data have been displaced vertically for clarity.

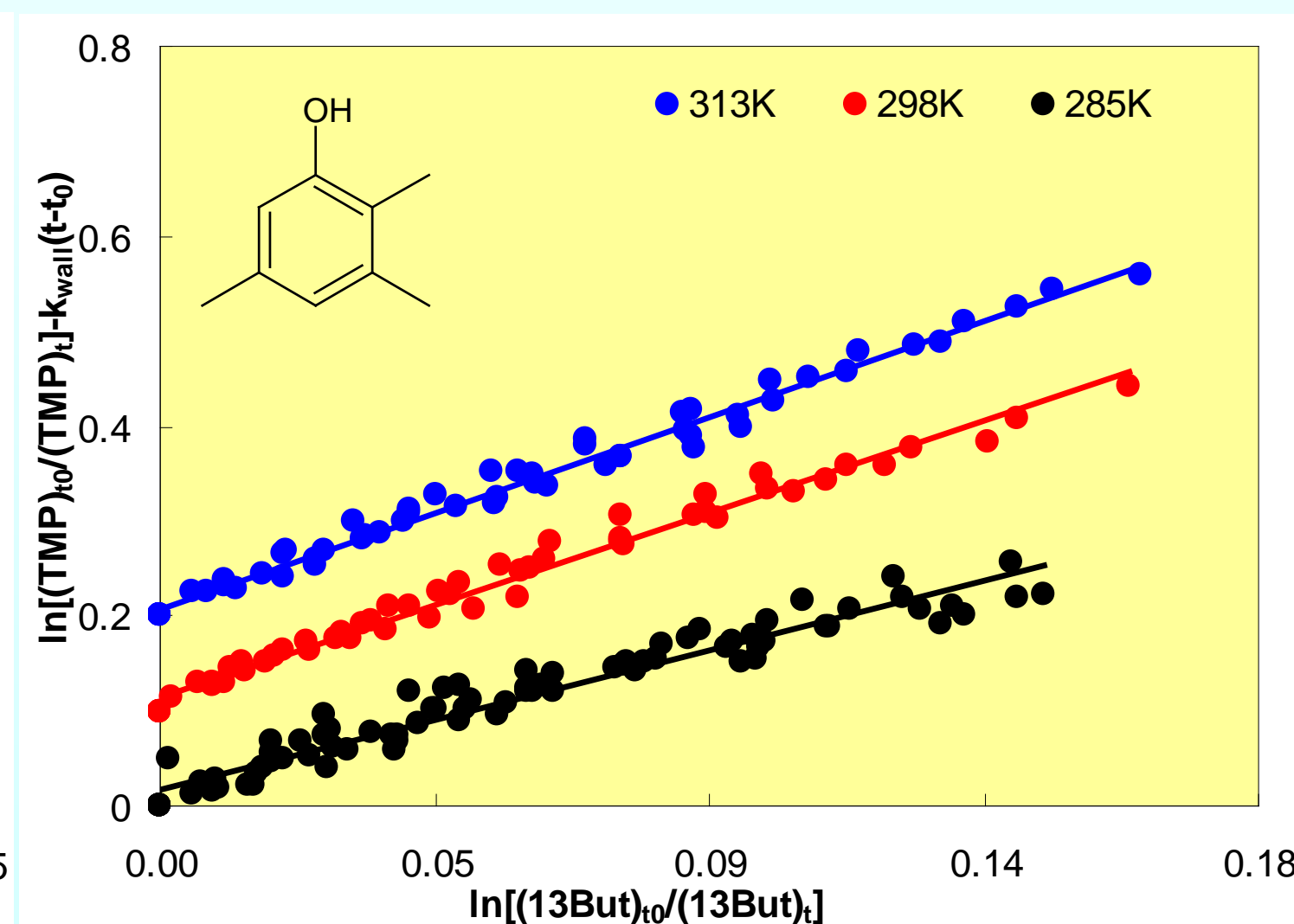


Fig. 3. Kinetic data plotted according to eq (1) for the reaction of OH radicals with 235TMP at different temperatures using 1,3-butadiene as reference hydrocarbon. The data have been displaced vertically for clarity.

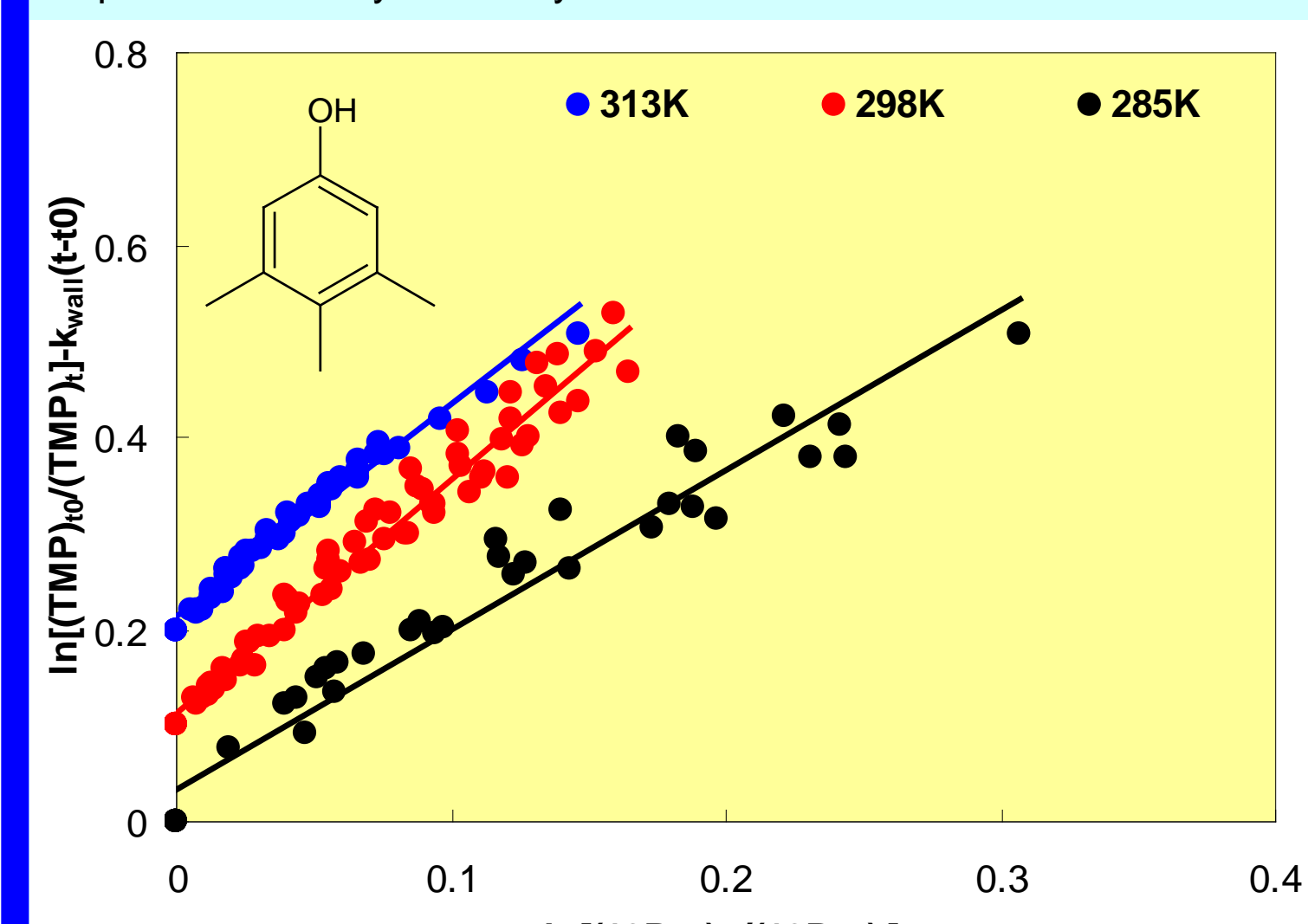


Fig. 4. Kinetic data plotted according to eq (1) for the reaction of OH radicals with 345TMP at different temperatures using 1,3-butadiene as reference hydrocarbon. The data have been displaced vertically for clarity.

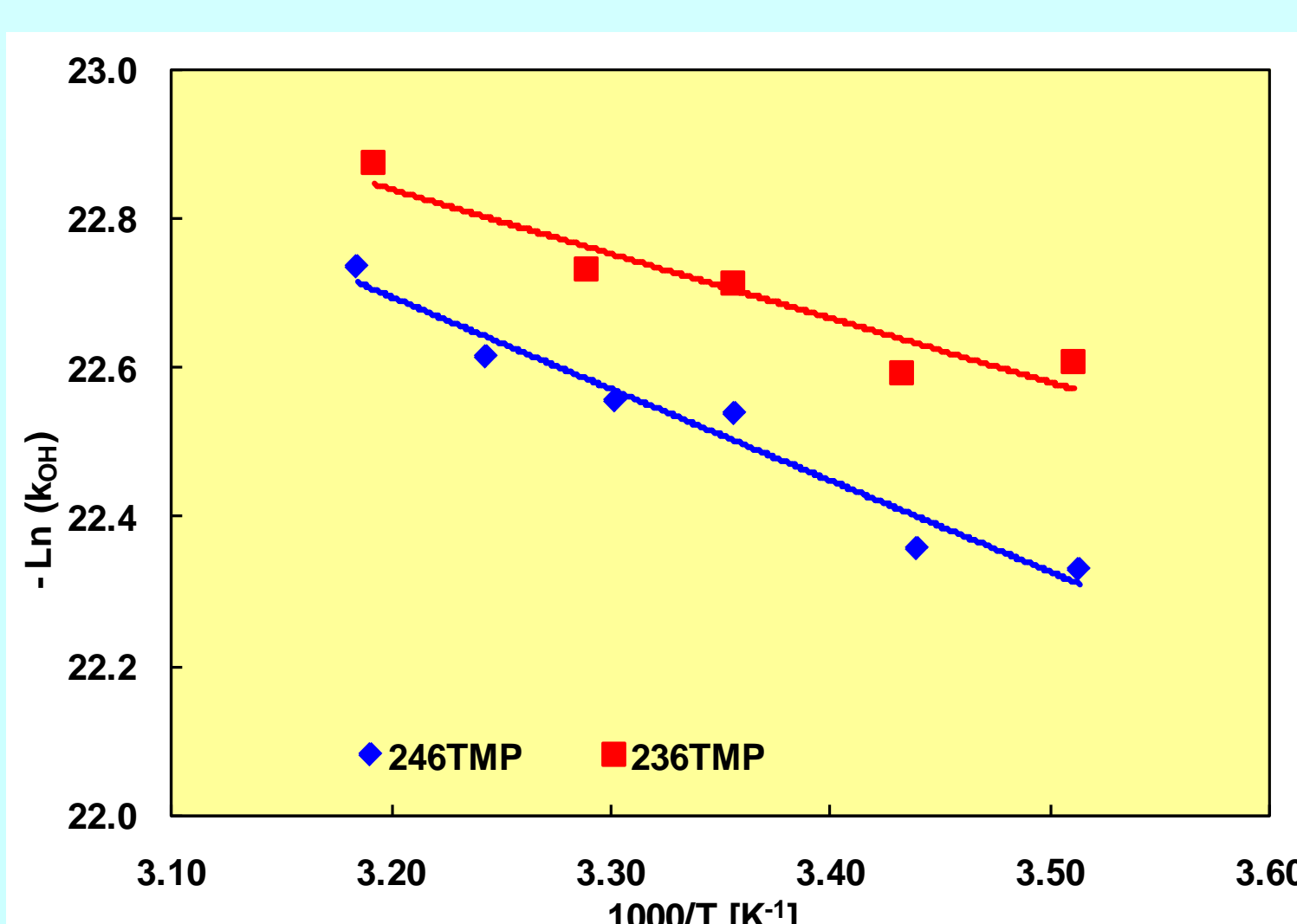


Fig. 5. Arrhenius plot of the rate coefficients for the reaction of OH radicals with 236TMP (■) and 246TMP (●).

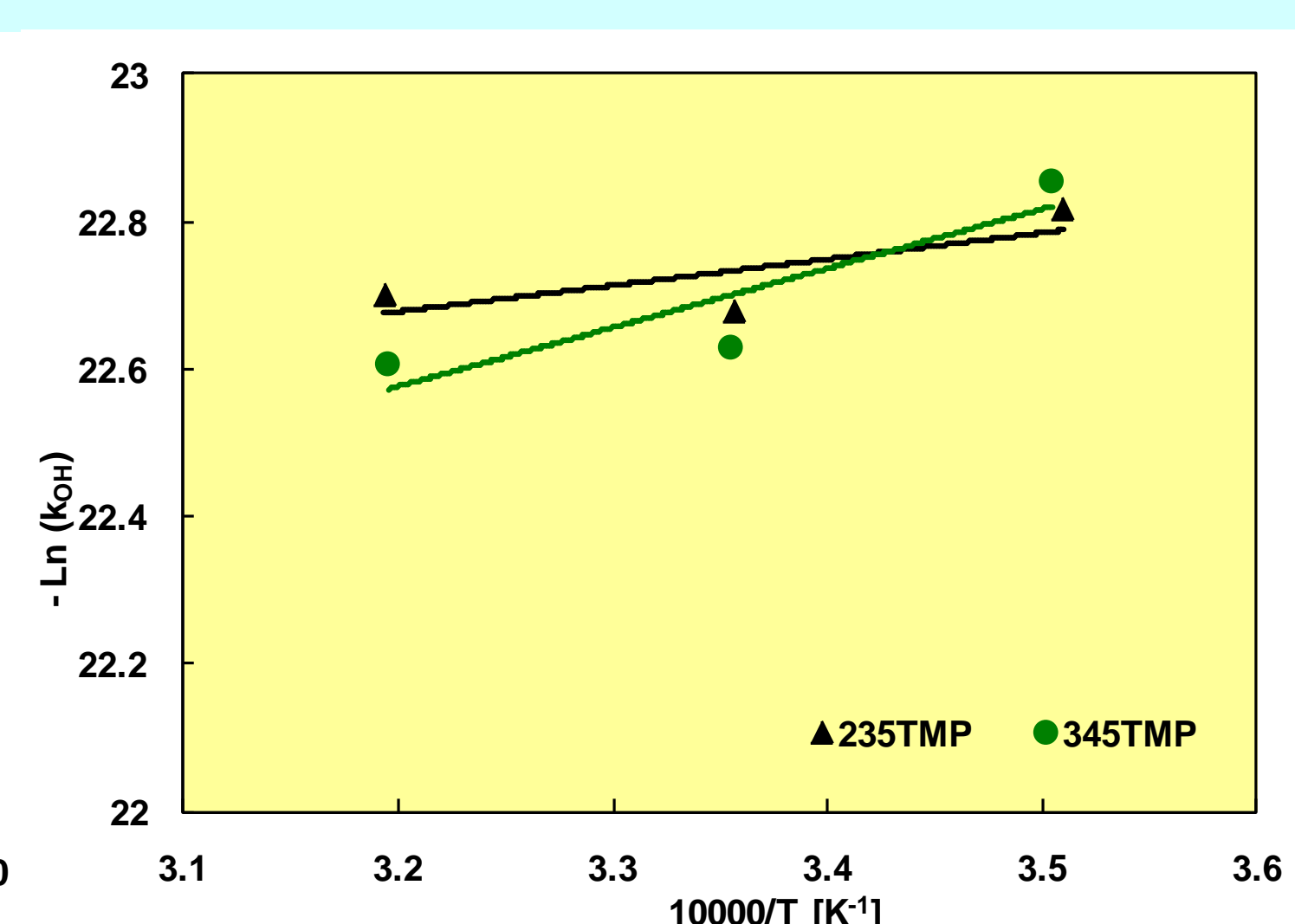


Fig. 6. Arrhenius plot of the rate coefficients for the reactions of OH radicals with 235TMP (▲) and 345TMP (●).

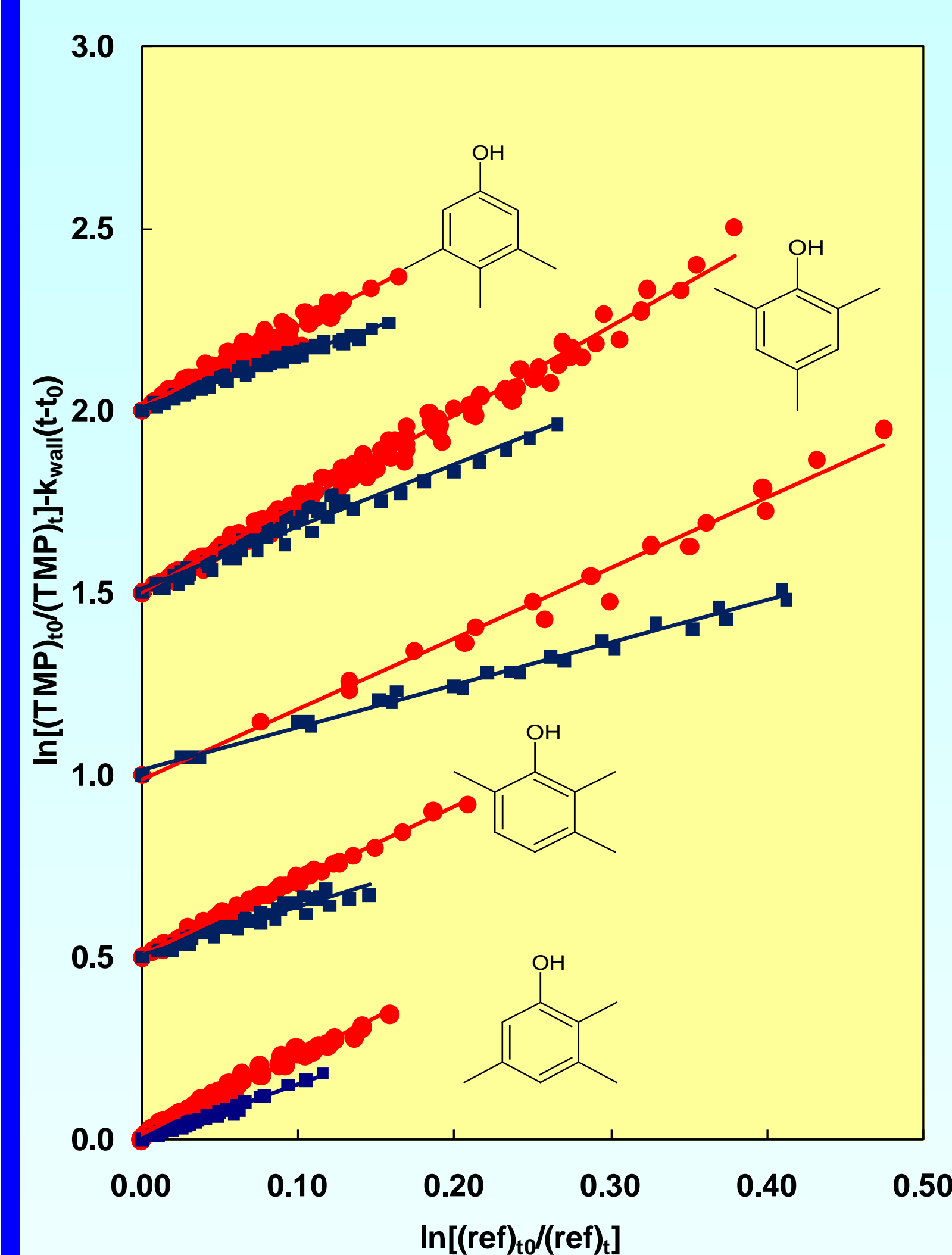


Fig. 7. Kinetic data plotted according to eq (1) for the reactions of OH radicals with 235TMP, 236TMP, 245TMP, 246TMP and 345TMP, using 1,3-butadiene (●) and isoprene (■) as reference hydrocarbons.

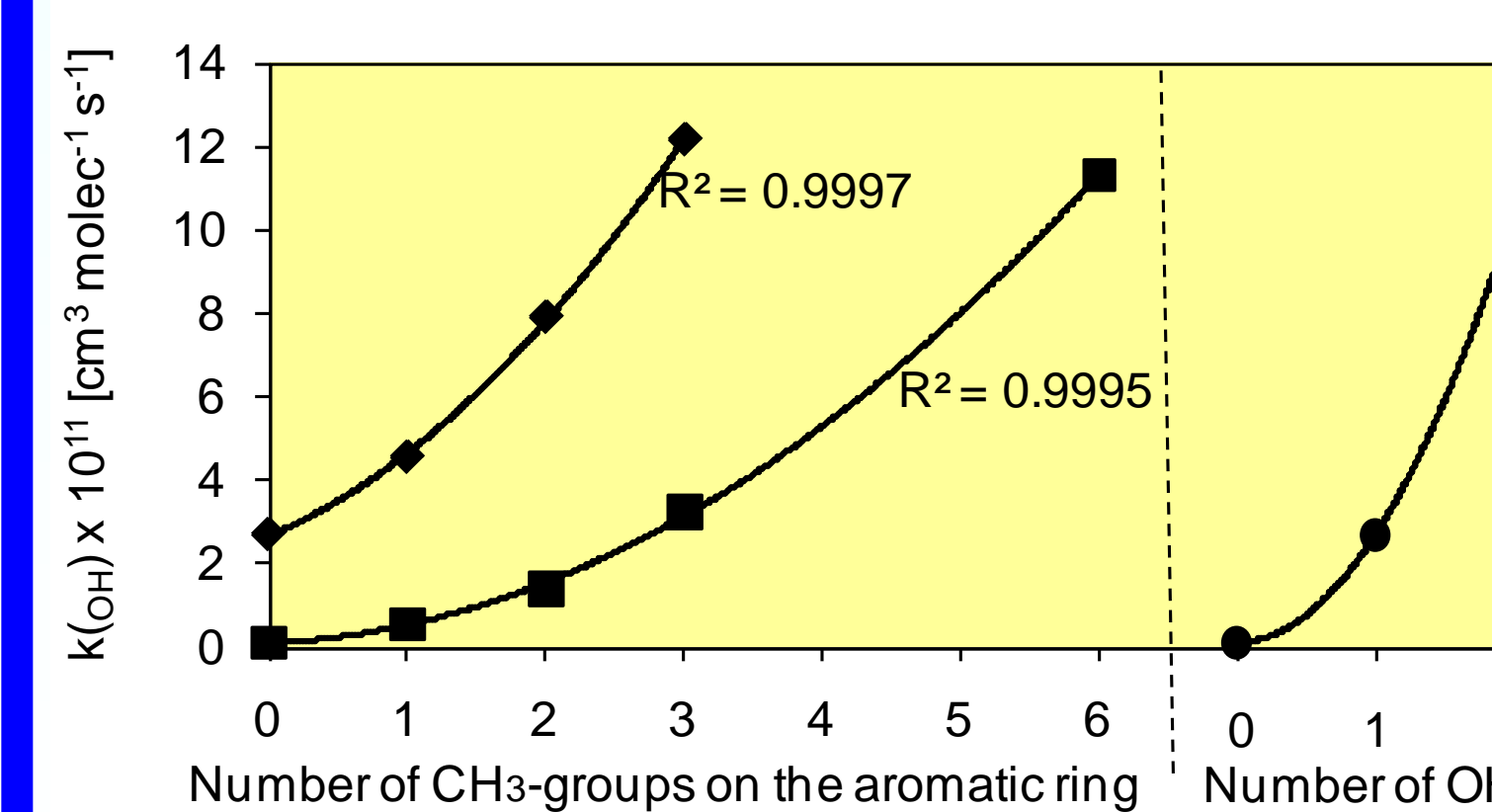


Fig. 8. Trends in rate coefficients for the reaction of OH with methylated benzenes, methylated phenols and hydroxylated benzenes: effect of CH₃ group addition to the benzene ring (■), effect of CH₃ group addition to the phenolic ring (●), effect of OH group addition to the benzene ring (▲) (Calvert et al., 2002).

Table 1. Rate coefficients for the reactions of OH radicals with four trimethylphenols in the temperature range 283 to 313 K. Reference hydrocarbons: 1,3-butadiene; $k(13\text{Butadiene})=1.58 \pm 0.07 \times 10^{-11} \exp [436 \pm 13/T]$ (Li et al., 2006) and isoprene; $k(\text{isoprene})=1.00 \pm 0.2 \times 10^{-10}$ (Atkinson et al., 2006). Average and literatures are at 298 K.

Trimethyl phenol	reference	temperature	k_1/k_2	$k_{\text{TMP}} \times 10^{-11}$ [cm ³ ·molec ⁻¹ ·s ⁻¹]	$k_{\text{TMP average}} \times 10^{-11}$ [cm ³ ·molec ⁻¹ ·s ⁻¹]	$k_{\text{TMP literature}} \times 10^{-11}$ [cm ³ ·molec ⁻¹ ·s ⁻¹]
2,4,6-TMP	1,3-butadiene	285±1	2.80±0.08	(20.0±1.04)	(16.7±1.60)	(13.1±1.5) Volkamer et al. (2001)
		291±1	2.82±0.06	(19.5±0.86)		
		298±1	2.44±0.05	(16.3±0.80)		
		303±1	2.46±0.03	(16.0±0.20)		
		308±1	2.38±0.03	(15.1±0.12)		
		314±1	2.17±0.02	(13.4±0.08)		
2,3,6-TMP	1,3-butadiene	285±1	2.13±0.07	(15.2±1.02)	(13.5±1.40)	(11.8±1.8) Tse et al. (1997)
		291±1	2.24±0.08	(15.4±1.11)		
		298±1	2.05±0.04	(13.6±0.54)		
2,3,5-TMP	1,3-butadiene	285±1	1.63±0.08	(14.4±0.81)	(14.8±1.41)	(12.5±1.9) Tse et al. (1997)
		298±1	2.16±0.07	(14.4±1.11)		
		313±1	2.24±0.07	(11.7±0.88)		
3,4,5-TMP	1,3-butadiene	285±1	1.66±0.13	(11.9±0.48)	(15.5±1.92)	-
		298±1	2.44±0.11	(16.2±1.73)		
		313±1	1.63±0.09	(15.2±0.53)		
2,4,5-TMP	1,3-butadiene	298±1	1.94±0.12	(12.9±1.55)	(12.3±1.60)	-
		isoprene	298±1	1.17±0.05		

Table 2. Arrhenius parameters for the gas phase reactions of OH radicals with trimethylphenols. Comparison of the rate coefficients obtained in this work at 298 K with estimated values using AOP WIN. Lifetimes for the reactions of OH radicals with four trimethylphenols at 298 K. $\tau(\text{OH})=1/k_{\text{OH}}[\text{OH}]$ with $[\text{OH}]=1.6 \times 10^6$ radical cm⁻³ (Prinn et al., 2005)

Trimethyl phenol	A × 10 ⁻¹² [cm ³ ·molec ⁻¹ ·s ⁻¹]	B [K]	Ea [kJ mol ⁻¹]	$k_{\text{TMP average}} \times 10^{-11}$ [cm ³ ·molec ⁻¹ ·s ⁻¹]	$k_{\text{TMP estimated}} \times 10^{-11}$ [cm ³ ·molec ⁻¹ ·s ⁻¹]	$\tau(\text{OH})$ [h]
2,4,6-TMP	(2.73±2.32)	-1229±254	(-10.22±2.1)	(16.7±1.60)	2.40 × 10 ⁻¹¹	1.04
2,3,6-TMP	(7.59±8.73)	-864±342	(-7.19±2.85)	(13.5±1.40)	13.1 × 10 ⁻¹¹	1.29
2,3,5-TMP	(7.85±23.86)	530±907	(4.41±7.5)	(14.8±1.41)	20.1 × 10 ⁻¹¹	1.17
3,4,5-TMP	(2.07±10.08)	798±1451	(6.64±12.06)	(15.5±1.92)	20.1 × 10 ⁻¹¹	1.12
2,4,5-TMP				(12.3±1.60)	13.1 × 10 ⁻¹¹	1.41
2,3,4-TMP					13.1 × 10 ⁻¹¹	

LITERATURE

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EXPERIMENTAL SETUP

OH kinetic

The OH radical kinetic measurements were performed in a 1080 L photoreactor. A White type multiple reflection mirror system operated at a total optical path length of (484.7 ± 0.8) m coupled to a NEXUS FTIR spectrometer was used for reactant and reference monitoring. The chamber is described in detail elsewhere (Mihalopoulos et al., 1992) (see Figure 9). The photolysis of CH₃ONO with 32 super-actinic fluorescent lamps in the presence of air was used as the OH radical source:

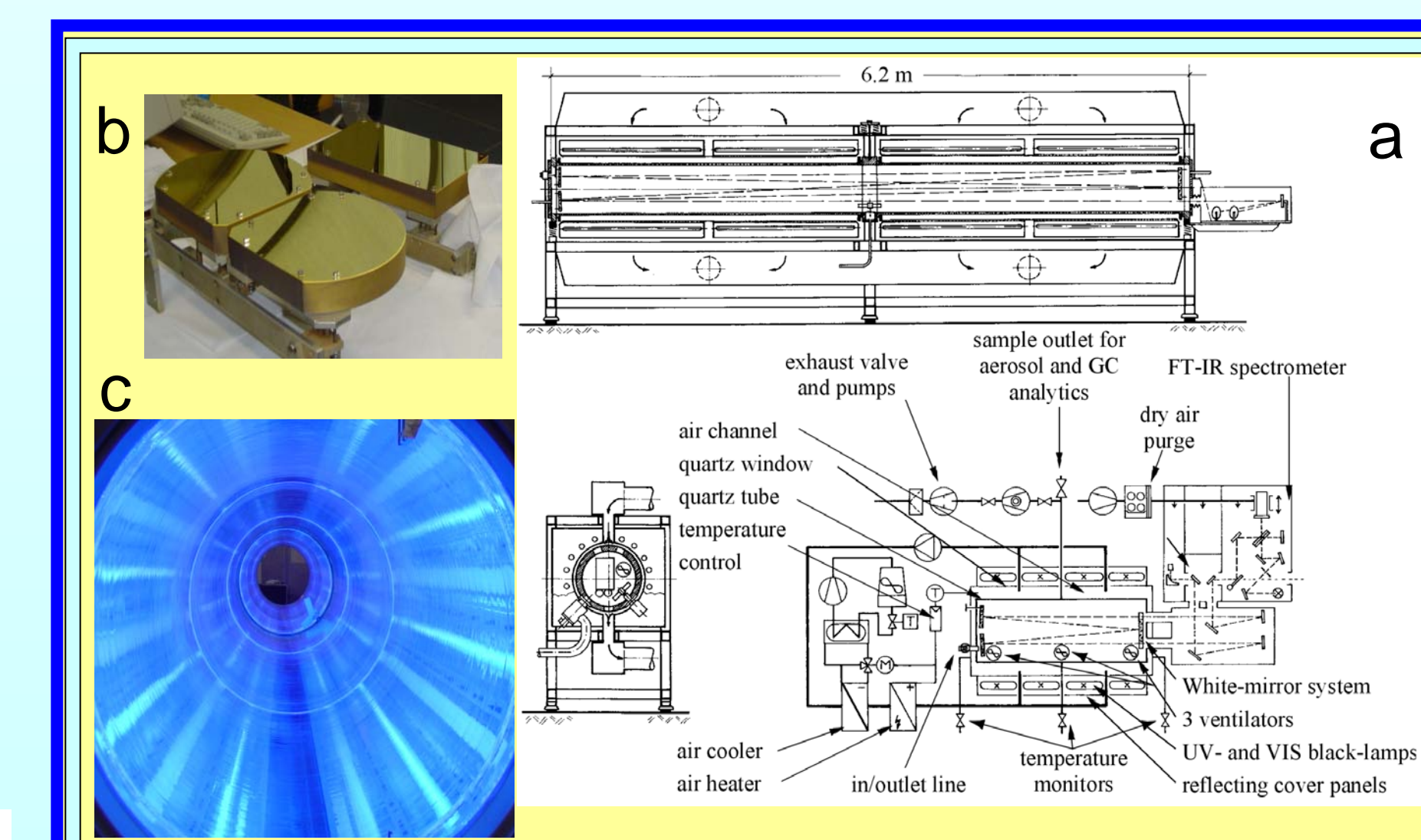
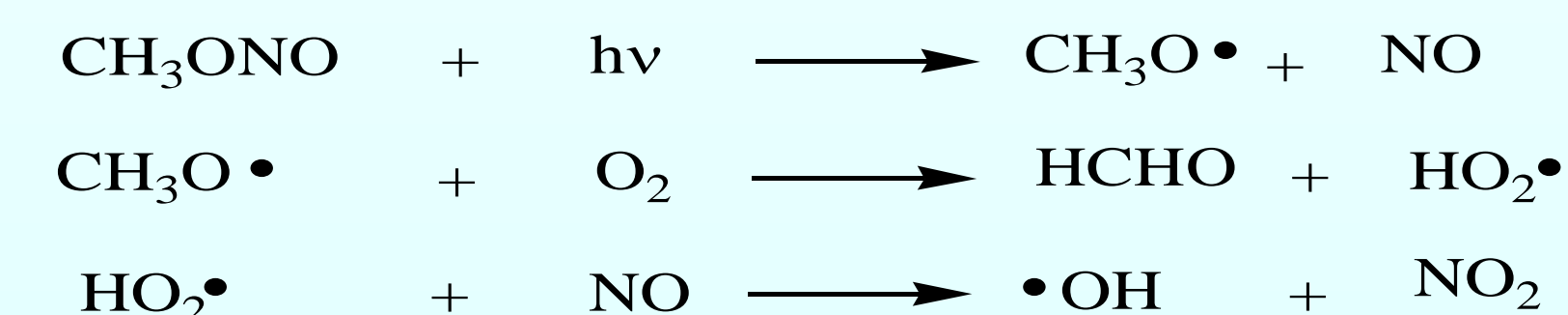
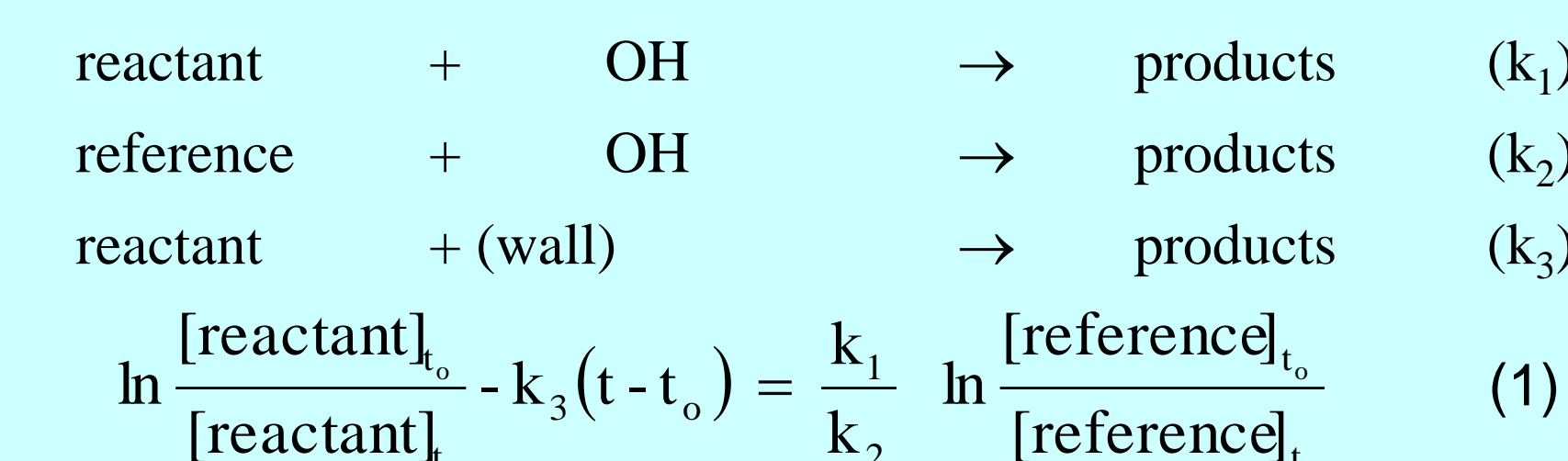


Fig. 9. a) Reactor experimental setup; b) White-type multiple reflection mirrors; c) Inner view of the tubular 1080L quartz glass reactor

Relative rate kinetic

The experimental data are plotted in Figures 1 - 4 and 7 according to eq (1).



CH₃ONO (~2 ppmV), isoprene (0.9 ppmV), 1,3-butadiene (0.9 ppmV) were injected into the reactor under reduced pressure using calibrated gas-tight syringes; trimethylphenols (0.1 – 0.4 ppmV) were introduced into the chamber in an air flow using a special heated inlet system.

REMARKS

All the kinetic plots show good linearity considering the difficulties which arise in the study of these aromatic systems;

First reported kinetic study of the reaction of OH radicals with 345-trimethylphenol and 245-trimethylphenol;

First reported temperature dependence kinetic study of the reaction of OH radicals with trimethylphenol isomers;

Very good agreement between the rate coefficients obtained using two different reference hydrocarbons (1,3-butadiene and isoprene);

For 235-trimethylphenol and 345-trimethylphenol a near zero (but potentially slightly positive) temperature dependence is observed for reaction with OH over the temperature range 283 – 313 K;

For 236-trimethylphenol and 246-trimethylphenol a definite slightly negative temperature dependence is observed. Such a temperature behaviour has also been measured for cresols;

The near zero or slightly positive trends in temperature dependence are observed for the trimethylphenol isomers in which at least one ortho position to the OH is not occupied (235- and 345-TMP) while the slightly negative trends are observed for the trimethylphenols with both ortho positions occupied, i.e. 246- and 236-TMP

As seen in Figure 8, the consecutive addition of a methyl group to the aromatic ring increases the reactivity of the AH toward OH radical reaction. The addition of OH to the AH ring is probably favoured by the electron-donating effect of the methyl group. However, from recent kinetic and product studies on the reaction of hexamethylbenzene with OH it can not be excluded that ipso addition of the OH radical may be important;

Product studies are necessary to determine the reaction mechanism.

ACKNOWLEDGEMENT

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