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Authors

Finlayson-Pitts, B. J
Ezell, M. J
Jayaweera, T. M
et al.

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KINETICS OF THE REACTIONS OF OH WITH METHYL CHLOROFORM AND METHANE:
IMPLICATIONS FOR GLOBAL TROPOSPHERIC OH AND THE METHANE BUDGET

B. J. Finlayson-Pitts, M. J. Ezell, T. M. Jayaweera, H. N. Berko and C. C. Lai

Department of Chemistry & Biochemistry, California State University, Fullerton

Abstract. The hydroxyl radical plays a central role in the oxidation of methane, larger organics including methyl chloroform, and CO in the troposphere. Hence a knowledge of the kinetics of such reactions is essential in estimating atmospheric lifetimes of these organics as well as global OH concentrations. We report here fast flow discharge studies of the absolute rate constants for both the OH-CH₃CCl₃ and OH-CH₄ reactions from 278-378 K in He at 1.05±0.05 Torr pressure. For CH₃CCl₃, $k(\text{CH}_3\text{CCl}_3) = (9.1^{+4.6}_{-3.7} \times 10^{-13}) \exp[-(1337 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ). The rate constants at 298 K and 277 K, 1.0 and 0.73×10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ respectively, are approximately 15% and 5% below the values now used to estimate global OH concentrations. The use of these lower rate constants in computations of global OH based on CH₃CCl₃ emissions and ambient measurements will increase the estimated OH concentrations, particularly at higher temperatures found in warmer equatorial regions. For CH₄, $k(\text{CH}_4) = (4.0^{+1.6}_{-1.3} \times 10^{-12}) \exp[-(1944 \pm 114)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (2σ). At 298 K and 277 K respectively, this gives values which are ~23% and 28% below the values which have generally been used in tropospheric models. Our results therefore support the recent suggestion that the methane flux may have been overestimated in the past.

Introduction

Tropospheric oxidation of saturated organics is primarily due to reaction with OH [Finlayson-Pitts and Pitts, 1986]. Hence, accurate knowledge of the kinetics of the OH reactions with such species is important for calculating the tropospheric lifetimes and fluxes of volatile organic compounds. For example, one recent study [Vaghjiani & Ravishankara, 1991] (referred to hereafter as V & R) reported a rate constant for the OH + CH₄ reaction which is ~19% lower at 273 K than previous values [Atkinson, 1989; DeMore et al, 1990], suggesting that the methane flux has been overestimated by ~20%.

Another important use of such rate constants is to estimate global OH concentrations. Many such estimates of global OH have been based on measured tropospheric CH₃CCl₃ concentrations [Singh, 1977; Lovelock, 1977; Makide & Rowland, 1981; Logan et al, 1981; Chameides & Tan, 1981; Prinn et al, 1983, 1992; Khalil & Rasmussen, 1984; Fraser et al, 1986; Spivakovsky et al, 1990] and a knowledge of its emissions [Midgley, 1989] and reaction kinetics with OH [Atkinson, 1989; DeMore et al, 1990; Atkinson et al, 1992].

Given the importance of accurately knowing the absolute values of the OH + CH₃CCl₃ and OH + CH₄ rate constants, we have reexamined their reaction kinetics from 278-378K.

Experimental

A fast flow discharge system coated with halocarbon wax or phosphoric acid and equipped with resonance fluorescence detection of OH [Kleindienst & Finlayson-Pitts, 1979] was used. OH in the range (0.5-1.5)×10¹² cm⁻³ was generated from the H + NO₂ reaction. Organic concentrations ranged from (2-

30) ×10¹⁴ molecules cm⁻³. The total pressure was 1.05±0.05 Torr in He carrier gas.

The purity of CH₃CCl₃ is critical to the accurate determination of the OH + CH₃CCl₃ rate constants. The presence of only 0.1% 1,1-dichloroethene will increase the measured rate constant at 298 K by 100%. The CH₃CCl₃ (Aldrich anhydrous 99+%, stabilized with 0.05% low alkyl epoxide) was carefully purified by: (1) refluxing under N₂ to prevent possible O₂ oxidation while stirring with 98% H₂SO₄ to react the epoxide and the olefin, (2) washing with 10% Na₂CO₃ or NaHCO₃ followed by distilled deionized water, (3) drying over Na₂SO₄, (4) distilling under N₂ into 3-5 fractions, each being analyzed by GC for the lowest olefin content prior to use in the kinetic experiments. The only remaining impurities were small amounts (<0.004%) of 1,1- and 1,2-dichloroethane which will not interfere with the kinetic measurements, and 1,1-dichloroethene, which varied from <0.0002- 0.003%. Using published kinetics [Kirchner et al, 1990; Zhang et al, 1991; Abbott & Anderson, 1991] the maximum contribution of the alkene to the measured rates was only 5% at 278 K and 3% in one set of runs at 298 K, for which the reported data have been corrected. For all other runs, the contribution of the alkene was ≤1% and no corrections were made. Analysis of the methane (Matheson, either UHP grade, >99.97% or Research Purity, >99.99%) by GC established it contained < 0.5 ppm ethene. Propene (< 2 ppm by manufacturer's specifications) was undetectable. Flows of both organics were calculated from the measured pressure drops in a calibrated volume during each experiment.

In a great excess of organic, the decay of OH was followed by the measured decrease in its resonance fluorescence intensity (I_f) at time t from the initial value, I₀, at t=0:

$$\ln \frac{[\text{OH}]}{[\text{OH}]_0} = \ln \frac{I_f}{I_0} = -(k_x[\text{X}]_0 + k_w)t$$

X = CH₃CCl₃ or CH₄, k_x is the corresponding rate constant for reaction with OH, and k_w is the loss of OH at the flow tube walls. The rate constant, k_x, is derived by plotting the slopes of 5-7 plots of ln I_f versus reaction time against [X]₀. Weighting procedures for ln I_f versus t as recommended by Cvetanovic et al [1975] were used. For the Arrhenius plots of ln k versus T⁻¹, ln k was weighted by w_i = k_i²w_i where w_i = (1/σ²) as recommended by Cvetanovic and Singleton [1977]. As seen in Figure 1, plots of ln I_f versus reaction time were linear, but do not have a common intercept of ln I₀ at t=0 as expected, due to collisional quenching of the electronically excited OH(A²Σ⁺) by the relatively large concentrations of organic added. The ratio of the observed intensity at t=0 expected in the absence of electronic quenching, I₀^{Q=0}, to that when quenching occurs, I₀, is given by (I₀^{Q=0}/I₀) = [(k_r+k_Q[X]₀)/k_r]. If N is the intercept of plots such as Figure 1 of ln I_f versus reaction time, then I₀ = e^N and e^{-N} = (1/I₀^{Q=0}) [1+(k_Q[X]₀/k_r)]. The value of k_Q/k_r can then be obtained from the ratio of the slope to intercept of plots of e^{-N} against [X]₀.

Results and Discussion

The results for both the reaction of OH with CH₄ and with CH₃CCl₃ are summarized in Table 1. Figures 2 and 3 show ln k versus T⁻¹ for each reaction; within the precision of the data, a

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Fig. 1 Typical decays of OH resonance fluorescence intensity in the presence of varying concentrations of methyl chloroform (in units of 10^{14} molecules cm^{-3}). Flow tube wall coating is halocarbon wax, $T = 298$ K.

Table 1. Summary of rate constants^a for the reactions of OH with CH₄ and CH₃CCl₃.

T (K)	Wall Coating	Range of k_w (s^{-1})	k ($\pm 2\sigma$) ($10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	k_Q/k_T ($\pm 2\sigma$) ($10^{-16} \text{ cm}^3 \text{ molec}^{-1}$)
OH + CH₄				
378	Acid (6) ^b	3-12	2.36 ± 0.08	2.0 ± 0.3
363	Acid (4)	8-12	2.05 ± 0.19	2.2 ± 0.3
348	Wax (4)	3-6	1.43 ± 0.36	1.7 ± 0.3
	Acid (3)	4-8	1.50 ± 0.25	1.5 ± 0.5
333	Wax (2)	4	1.09 ± 0.06	1.4 ± 0.5
	Acid (4)	4-10	1.05 ± 0.28	2.0 ± 0.5
313	Wax (2)	7-8	0.792 ± 0.007	1.6 ± 0.1
	Acid (4)	6-11	1.06 ± 0.17	1.4 ± 0.3
298	Wax (2)	4-8	0.575 ± 0.098	1.9 ± 0.1
	Acid (8)	2-8	0.560 ± 0.063	1.7 ± 0.1
278	Wax (3)	8-10	0.409 ± 0.026	1.9 ± 0.3
OH + CH₃CCl₃				
378	Acid (5)	0-45	2.68 ± 0.28	6.3 ± 0.9
358	Acid (3)	1-3	2.17 ± 0.11	5.3 ± 0.5
348	Wax (4)	1-5	1.87 ± 0.25	5.4 ± 0.6
338	Acid (4)	4-24	1.99 ± 0.24	5.4 ± 0.8
333	Wax (4)	5-8	1.61 ± 0.16	5.5 ± 0.5
318	Wax (4)	6-8	1.28 ± 0.09	5.5 ± 0.4
	Acid (4)	5-18	1.38 ± 0.42	6.1 ± 1.1
298	Wax (4)	6-10	0.911 ± 0.098^c	5.4 ± 0.3
	Acid (5)	8-15	1.12 ± 0.16	5.8 ± 1.4
278	Wax (6)	10-15	0.789 ± 0.074^d	5.1 ± 0.3

^aRate constants are weighted averages using weights [Cvetanovic & Singleton, 1977] of $w=1/\sigma^2$, where σ is one standard deviation of the value of k measured in each run. All data have been corrected for axial and radial diffusion (typically <5% correction) using the method of Brown [1978].

^bNumbers in parentheses are number of individual experiments performed; Acid=phosphoric acid coating; Wax=halocarbon wax coating

^cCorrected by 3% for contribution of 1,1-dichloroethene

^dCorrected by 5% for contribution of 1,1-dichloroethene

Fig. 2 Plot of $\ln k$ versus T^{-1} for the reaction of OH with CH₄. ● halocarbon wax wall coating X phosphoric acid wall coating. The dot-dash line is the 1990 NASA recommendation [DeMore et al, 1990] and the dashed line is from Vaghjiani and Ravishankara [1991] whose two parameter fit gives $A=(2.94 \pm 0.34) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_a/R = (1815 \pm 30) \text{ K}$.

Fig. 3 Plot of $\ln k$ versus T^{-1} for the reaction of OH with methyl chloroform. ● halocarbon wax wall coating X phosphoric acid wall coating. Dashed line is recommendation of Atkinson [1989] and DeMore et al [1990] and Atkinson et al [1992], based on the work of Jeong and Kaufman [1979] and Kurylo et al [1979], which is used in most current tropospheric models.

good fit to the two parameter form $k = Ae^{-(E_a/RT)}$ could be obtained over this temperature range.

Our Arrhenius expression for the OH + CH₄ reaction, $k = (4.0^{+1.6}_{-1.3} \times 10^{-12}) \exp[-(1944 \pm 114/T)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (2\sigma)$, gives rate constants that are within experimental error of the recent temperature dependence of V&R but below the recommended values of DeMore et al (1990) used in most current tropospheric models. For example, our value at 277 K, relevant for calculating tropospheric lifetimes [Prather & Spivakovsky, 1990], is $3.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, significantly lower than the DeMore et al (1990) recommendation of 5.0×10^{-15} but within 10% of the recent V&R value of $4.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Our Arrhenius parameters are thus in excellent agreement with the most recent IUPAC recommendations, $A = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_a/R = 1885 \text{ K}$, which are based in part on the V&R data.

Vaghjiani and Ravishankara [1991] attributed the larger rate constants reported earlier to the use of higher initial [OH] which can cause secondary reactions, such as that of OH with CH₃. This could become especially important at lower [CH₄]/[OH] ratios. However, the only published estimate for $k(\text{CH}_3 + \text{OH})$, $9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was obtained indirectly at room temperature and one atmosphere pressure in a complex system [Sworski et al, 1980] and hence may not be applicable at lower pressures if the rate constant is pressure dependent. The excellent agreement of the present results obtained at 1 Torr, $[\text{OH}]_0 \sim 1 \times 10^{12} \text{ radicals cm}^{-3}$ and $[\text{CH}_4]/[\text{OH}] \sim 10^3$, with those of V&R at 100–300 Torr, $[\text{OH}]_0 = (0.14\text{--}1.9) \times 10^{12} \text{ radicals cm}^{-3}$ and $[\text{CH}_4]/[\text{OH}] \sim 10^5\text{--}10^6$, combined with computer kinetic modelling studies using their mechanism and the algorithm of Braun et al [1988], suggests that under our conditions such secondary reactions are not important.

The precision which can be obtained with a fast flow discharge system in studying relatively slow reactions is typically 15% (2 σ). However, while higher precision can be obtained using other techniques, it is important for the ultimate accuracy of rate constants that a variety of methods encompassing different reaction conditions be applied. The good agreement between our results and those of V&R confirm that the OH + CH₄ rate constants used in previous tropospheric models may indeed be too large and hence methane fluxes are overestimated as they suggested.

The data for the OH + CH₃CCl₃ reaction can be fitted to $k = (9.1^{+4.6}_{-3.9} \times 10^{-13}) \exp[-(1337 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (2\sigma)$ with $k^{298} = (1.0 \pm 0.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, ~15% below the currently recommended value of $(1.19 \pm 0.36) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Atkinson, 1989; DeMore et al, 1990; Atkinson et al, 1992]. The temperature dependence also differs significantly from the earlier studies (Table 2), but is in better agreement with an absolute kinetics study carried out in parallel with this work [Talukdar et al, 1992]. Our values for the ratios of rate constants $k^{\text{CH}_3\text{CCl}_3}/k^{\text{CH}_4} = 1.7$ and 2.0 at 298 K and 277 K respectively, are also in good agreement with ratios of 1.65 and 1.77 obtained in recent relative rate studies [DeMore, 1992].

Possible reasons for the difference between our results and the earlier studies lie in the difficulty in handling CH₃CCl₃ and quantifying its concentrations. It tended to adhere to the walls of the vacuum system, and was observed to form 1,1-dichloroethene on contact with a metal gas sampling valve. Olefins would increase the measured rate constants and decrease the steepness of the temperature dependence. However, during our kinetic experiments, we carefully measured the amount of olefinic impurity before, during and after the runs to make certain the purified CH₃CCl₃ did not change during storage. In addition, experiments were done to ensure that the transfer of CH₃CCl₃ was quantitative, i.e. that the flow rates obtained from the decrease in pressure in a calibrated volume agreed with those based on the pressure increase in a receptor volume.

From the intercept of plots such as Figure 1, and using $k_t = 1.44 \times 10^6 \text{ s}^{-1}$ [German, 1975], the quenching rate constant of

Table 2. Summary of kinetic studies^a for reaction of OH with CH₃CCl₃.

$10^{14} k^{298}$ ($\text{cm}^3 \text{ s}^{-1}$ molec^{-1})	E_a/R (K)	$10^{12} A$ ($\text{cm}^3 \text{ s}^{-1}$ molec^{-1})	Reference
1.17	1832 $\pm$ 98	5.49 $\pm$ 1.40	Jeong & Kaufman
1.24	1810 $\pm$ 100	5.4 $\pm$ 1.8	Kurylo et al
1.3 ^b	1797 $\pm$ 448	5.4 $\pm$ 3	Nelson et al
1.09 ^c	—	—	Nelson et al
0.95	1550 $\pm$ 60	1.75 $\pm$ 0.34	Talukdar et al
1.0	1337 $\pm$ 150	0.91 $\pm$ 0.46 -0.37	This work

^aStudies prior to these have been discounted in recent kinetic evaluations [Atkinson, 1989; DeMore et al, 1990; Cohen & Westberg, 1991; Atkinson et al, 1992] because of the contribution of olefinic impurities.

^bExtrapolated from absolute rate data in the range 359–402 K.

^cRelative rate technique taking $k(\text{CH}_3\text{Cl}) = 4.36 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

OH ($A^2\Sigma^+$) by CH₄ was $k_Q = (2.6 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in excellent agreement with the rotational level specific rate constants of Copeland et al [1985] which vary from $(3.1\text{--}2.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $N = 0\text{--}7$. k_Q for quenching by CH₃CCl₃, $(8.1 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is slightly lower than the value of $(11.1 \pm 0.7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Clyne and Holt [1979]. Within experimental error, there was no discernible temperature dependence of the ratio k_Q/k_t for collisional quenching of OH($A^2\Sigma^+$) by either CH₃CCl₃ or CH₄ from 278–378 K. As expected, quenching of OH by polar CH₃CCl₃ is faster due to the larger attractive forces [Copeland et al, 1985].

Use of our less steep temperature dependence for the OH + CH₃CCl₃ reaction compared to that currently used to calculate tropospheric OH levels will change the computed OH geographical distribution. Thus, application of our rate expression to warmer equatorial regions where our rate constant is smaller (by ~15% at 298 K) will lead to higher calculated OH concentrations in these regions, with correspondingly shorter lifetimes for organics and CO.

Given the importance of the OH + CH₃CCl₃ reaction, additional kinetic, both relative and absolute, as well as mechanistic studies using the variety of kinetic techniques currently available are needed.

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H.N. Berko, M.J. Ezell, B.J. Finlayson-Pitts, T.M. Jayaweera and C.C. Lai, Department of Chemistry and Biochemistry, California State University, Fullerton, Fullerton, CA 92634.

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