Relative Rate Constants for the Reactions of Hydroxyl Radicals and Chlorine Atoms with a Series of Aliphatic Alcohols

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ABSTRACT: Rate constants for the gas-phase reactions of hydroxyl radicals and chlorine atoms with a series of alcohols have been determined by using the relative method. The experiments were performed at 295 ± 2 K and at 1 atmospheric pressure. The obtained values of the rate constants in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are as follows:

Alcohol	Rate Constants for OH with		Rate Constants for Cl with	
	Propane	Cyclohexane	Propane	Cyclohexane
Ethyl alcohol	3.40 ± 0.25	–	103 ± 4	96 ± 7
<i>n</i> -Propyl alcohol	5.47 ± 0.44	–	153 ± 13	147 ± 11
Isopropyl alcohol	5.31 ± 0.39	–	73.5 ± 3.7	82.7 ± 7.4
<i>n</i> -Butyl alcohol	8.66 ± 0.66	–	211 ± 11	223 ± 10
Isobutyl alcohol	9.08 ± 0.35	9.59 ± 0.45	182 ± 4	196 ± 11
<i>tert</i> -Butyl alcohol	1.11 ± 0.07	–	31.5 ± 2.4	34.1 ± 2.5
<i>n</i> -Pentyl alcohol	12.2 ± 1.0	12.4 ± 0.5	257 ± 25	258 ± 12
Isopentyl alcohol	13.8 ± 0.5	13.2 ± 1.1	237 ± 7	235 ± 9

The above relative rate constants are based on the values (in units of $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of $k(\text{OH} + \text{propane}) = 1.08$, $k(\text{OH} + \text{cyclohexane}) = 7.22$, $k(\text{Cl} + \text{propane}) = 131$ and $k(\text{Cl} + \text{cyclohexane}) = 307$. The results are compared with previous determinations. © 2002 Wiley Periodicals, Inc. *Int J Chem Kinet* 35: 81–87, 2003

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INTRODUCTION

Oxygenated volatile organic compounds play an important role in atmospheric chemistry. Their atmospheric photochemical transformations represent a major source of organic free radicals in the lower

atmosphere. They can influence the oxidative potential of the troposphere and enhance acidic deposition in remote areas by formation of organic acids. Alcohols are an important class of these oxygenated compounds. They are widely used as solvents, fuels, and fuel additives, and so a substantial proportion of them can then be emitted into the atmosphere. They are also formed in the troposphere by photooxidation of non-methane hydrocarbons. Some of them are directly emitted from vegetation and biomass burning. Alcohols in the atmosphere are mainly removed by photolysis and chemical reactions [1]. Since their reactions with O_3 and NO_3 as well as their photolysis are negligible, the gas-phase degradation of alcohols in the atmosphere is initiated largely by reaction with OH radicals.

Initiation of atmospheric oxidation by OH radicals of alcohols leads to the formation of formaldehyde, acetone, formates, and other oxygenated organic species, which are components of photochemical smog in urban areas [2]. Together with mechanistic information, accurate kinetic data are needed for the reactions of alcohols with hydroxyl radicals to assess their relative ozone formation potentials and their contribution to urban pollution.

Previous studies [3] have shown that the rate constants for the reactions of Cl atoms with certain hydrocarbons can be much larger than that of corresponding molecules with OH radicals. Even though Cl atoms are present in lower concentrations than OH radicals, their faster rates of reactions with hydrocarbons can make Cl atom reactions competitive with OH reactions [4]. A variety of modeling and laboratory studies have shown that chlorine atoms could be generated by sea salt reactions and oxidation of halocarbons in the troposphere [5]. Spicer et al. [6] predicted that maximum chlorine atom levels occur shortly after sunrise with a peak concentration of 1.3×10^5 atoms cm^{-3} in both the remote marine boundary layer and coastal urban areas, and suggested that chlorine atoms play a potential important role in the atmospheric chemistry of the marine boundary layer and coastal urban areas.

Relative and absolute rate constants for a large number of alkanes, haloalkanes, alkenes, haloalkenes, aromatics, alkynes, and oxygen-, nitrogen-, and sulfur-containing organics have been determined since the 1970s. However, the database for the oxidation of alcohols is not abundant. For example, there are relatively few reports on the rate constants for reactions of hydroxyl radicals with *n*-pentyl alcohol and isopentyl alcohol, and still no reports on the reaction of hydroxyl radicals with isobutyl alcohol. In this paper, the relative rate constants for the reactions of hydroxyl radicals and chlorine atoms with a series of alcohols are reported. The rate constants for the reactions of Cl atoms with

isobutyl alcohol and isopentyl alcohol as well as for the OH radicals with isobutyl alcohol are reported for the first time. It was hoped that such a systematic investigation would extend the database for the reactions of OH radicals and Cl atoms with oxygenated organics and provide structure-reactivity information on the reactions.

EXPERIMENTAL

Kinetic experiments were carried out at 295 ± 2 K and atmospheric pressure with bath gas of air, in an approximately 100-l Teflon bag reaction chamber, which is hung inside a dark cubic ligneous cabinet of about 1000 l. Aluminum foil covering the inside wall of the cabinet reflected the UV light so as to enhance the light efficiency as well as prevent UV light exit. A thermometer was used to monitor the temperature inside the chamber. Four lamps set on the inner wall of the cabinet were used as the photolysis light source. The number of lights controlled light intensity. Generally, the OH radicals were generated through photolysis of H_2O_2 by using two low-pressure mercury lamps (ZSZ-40, 40 W, Beijing KongHou Factory for complex material), which provided UV radiation with an intensity maximum around 253.7 nm; the chlorine atoms were generated through photodegradation of molecular chlorine by using two fluorescent lamps (30 W, Academy of Electric Lamp-House in Beijing), which provided UV radiation with an intensity maximum around 365 nm.

A mercury-free greaseless vacuum system was used for all the experiments. Pressure measurements were done with an MKS Baratron capacitance manometer, MKS 270B. Measured amounts of the reagents were flushed from Pyrex bulbs into the Teflon reaction chamber by a stream of compressed air, which was purified by passing it through a charcoal column to remove hydrocarbon compounds. A mass flow meter (range: 0–5000 ml min^{-1} , ShengYe Technology Company of Beijing) controlled the flow rate. The Teflon bag was vibrated gently in order to mix the reagents inside the bag, and the gas mixtures were allowed to mix for about 20 min before analysis. A gas chromatograph (SC1001, Sichuan Analytical Instrument Factory), equipped with a flame ionization detector, was used for all quantitative analysis. Gas-tight syringes were used to collect reaction mixtures from the Teflon bag. The alcohols in the reaction mixtures were separated on a 2 m $\times$ 3 mm Teflon column packed with GDX 103 (60–80 mesh).

Analysis of propane was carried out by using another $1.8 \text{ m} \times 3 \text{ mm}$ Teflon column packed with Porapak QS (80–100 mesh).

The OH radicals or Cl atoms generated in reaction (1) or (2) react with the alcohols and reference hydrocarbon, with rate constants k_{alc} and k_{ref} , respectively:

Provided that reaction with OH or Cl atoms is the only significant loss process for both reactant and reference compounds, the decay of the alcohol from $[\text{alcohol}]_0$ at time $t = 0$ to $[\text{alcohol}]_t$ at time t , and the simultaneous loss of the reference compound from an initial concentration of $[\text{ref}]_0$ to $[\text{ref}]_t$ at time t is given by Eq. (5):

$$\frac{k_{\text{alc}}}{k_{\text{ref}}} = \frac{\ln([\text{alcohol}]_0/[\text{alcohol}]_t)}{\ln([\text{ref}]_0/[\text{ref}]_t)} \quad (5)$$

Thus a plot of $\ln([\text{alcohol}]_0/[\text{alcohol}]_t)$ vs. $\ln([\text{ref}]_0/[\text{ref}]_t)$ should be a straight line passing through the origin and whose slope gives the ratio of rate constants $k_{\text{alc}}/k_{\text{ref}}$. The rate constant k_{alc} was derived from literature values of k_{ref} .

The chemicals used were ethyl alcohol ($\geq 95\%$), *n*-propyl alcohol ($\geq 99.0\%$), isopropyl alcohol ($\geq 99.5\%$), *n*-butyl alcohol ($\geq 98.0\%$), isobutyl alcohol ($\geq 98.0\%$), *tert*-butyl alcohol ($\geq 95\%$), *n*-pentyl alcohol ($\geq 95\%$), isopentyl alcohol ($\geq 95\%$), HCl (36–38%), and KMnO_4 ($\geq 99.5\%$). All these chemicals were the products of Beijing Chemical Plant; H_2O_2 ($\geq 30\%$, Tianjin Oriental Chemical Plant); cyclohexane ($> 99\%$); propane, standard gas with mixing ratio of 2370×10^{-6} (v/v) in nitrogen (National Research Center for Certified Reference Materials, China), N_2 (ultrahigh purity, $> 99.999\%$) and H_2 (ultrahigh purity, $> 99.999\%$) were products of Beijing Haipu Beifen Gases Industry Company. The gas chlorine was prepared by dropwise addition of HCl to KMnO_4 in our laboratory. All alcohols, cyclohexane, and chlorine were further purified by repeat freeze, pump, and thaw cycles and fractional distillation before use.

RESULTS

To obtain accurate rate constants of studied alcohol compounds by using the relative method, the key work was to separate alcohols from reference compounds, as well as alcohols and references from their degradation products during the course of photooxidation. Several

Figure 1 Plots of $\ln([\text{alcohol}]_0/[\text{alcohol}]_t)$ vs. $\ln([\text{propane}]_0/[\text{propane}]_t)$ for the reaction of OH with representative alcohols.

tests were performed to check if there was any interference with analysis of alcohols or the references before rate constant study. In all cases, neither the reference nor the photooxidation products could interfere with analysis of the studied alcohols or the references on our employed separation columns.

OH Rate Constants

Some tests indicated that the studied alcohols and references were photochemically stable, and the mixtures of the alcohols and references with H_2O_2 were also stable in the dark for several hours in the Teflon bag. The initial concentrations of alcohols and propane were both between 50–60 ppm, and 0.5 ml liquid H_2O_2 was injected into the chamber to produce OH radicals by UV irradiation. The linear regressions of the natural logarithm of the concentration ratios of alcohols studied using propane as reference are shown in Figs. 1 and 2. The rate constants for the reactions of OH radicals with the alcohols were calculated using the value of $k(\text{OH} + \text{propane}) = 1.08 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K [7] according to Eq. (5), and results are

Figure 2 Plots of $\ln([\text{alcohol}]_0/[\text{alcohol}]_t)$ vs. $\ln([\text{propane}]_0/[\text{propane}]_t)$ for the reaction of OH with representative alcohols.

Table I Rate Constants for OH Radicals with Alcohols at ~295 K Compared with Literature Data

Molecule	<i>T</i> (K)	K^a (10^{-12} cm ³ molecule ⁻¹ s ⁻¹)	Technique ^b	Reference ^c
Ethyl alcohol	295	3.50 ± 0.60	RR	[8]
	293	3.40 ± 0.17	FP-RA	[9]
	303	3.66 ± 0.42	RR	[10]
	296	3.33 ± 0.23	FP-RF	[11]
	295	3.32 ± 0.16	LP-LIF	[12]
	296	3.74 ± 0.37	FP-RA	[13]
	298	3.46 ± 0.52	RR	[3]
	298	3.04 ± 0.25	PR-KS	[3]
	295	3.40 ± 0.25	RR	This work I
<i>n</i> -Propyl alcohol	296	5.34 ± 0.29	FP-RF	[11]
	292	3.82 ± 0.33	RR	[14]
	298	5.50 ± 0.44	RR	[3]
	298	5.64 ± 0.48	PR-KS	[3]
	298	5.83 ± 0.18	LP-LIF	[15]
	295	5.47 ± 0.44	RR	This work I
Isopropyl alcohol	298	5.69 ± 1.09	PR-KS	[3]
	298	5.78 ± 0.75	RR	[3]
	296	5.81 ± 0.34	FP-RF	[11]
	298	5.17 ± 0.23	LP-LIF	[15]
	305	7.1 ± 2.2	RR	[16]
	295	5.31 ± 0.39	RR	This work I
<i>n</i> -Butyl alcohol	298	8.56 ± 0.70	RR	[3]
	298	7.80 ± 0.20	PR-KS	[3]
	296	8.31 ± 0.63	FP-RF	[11]
	282	6.8 ± 1.0	RR	[14]
	298	8.47 ± 0.34	LP-LIF	[15]
	295	8.66 ± 0.66	RR	This work I
Isobutyl alcohol	295	9.08 ± 0.35	RR	This work I
	295	9.94 ± 0.47	RR	This work II
<i>tert</i> -Butyl alcohol	295	1.0 ± 0.2	RR	[8]
	298	1.07 ± 0.08	FP-RF	[17]
	298	0.81 ± 0.17	DF-LIF	[18]
	298	1.08 ± 0.10	LP-LIF	[19]
	295	1.11 ± 0.07	RR	This work I
<i>n</i> -Pentyl alcohol	296	10.8 ± 1.1	FP-RF	[11]
	298	10.5 ± 1.3	RR	[3]
	298	12.0 ± 1.6	PR-KS	[3]
	295	12.2 ± 1.0	RR	This work I
	295	12.9 ± 0.5	RR	This work II
Isopentyl alcohol	298	13.1 ± 2.6	DF-LIF	[18]
	295	13.8 ± 0.5	RR	This work I
	295	13.7 ± 1.1	RR	This work II

^a Quoted errors represent 2σ from a least-squares analysis.^b RR, Relative Rate; FP-RA, Flash Photolysis Resonance Absorption; FP-RF, Flash Photolysis Resonance Fluorescence; LP-LIF, Laser Photolysis Laser-Induced Fluorescence; DF-LIF, Discharge Flow Laser-Induced Fluorescence; PR-KS, Pulse Radiolysis Kinetic Spectroscopy.^c This work I, propane as the reference hydrocarbon; This work II, cyclohexane as the reference hydrocarbon.

listed in Table I. Since there are few reports on the rate coefficients for the reactions of OH radicals with isobutyl alcohol, *n*-pentyl alcohol, and isopentyl alcohol, experiments were carried out by using cyclohexane as

another reference in order to ensure accurate rate coefficients for these compounds. The data are presented in Fig. 3. Using a rate constant of $k(\text{OH} + \text{cyclohexane}) = 7.22 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 295 K [20], the rate

Figure 3 Plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([cyclohexane]_0/[cyclohexane]_t)$ for the reaction of OH with representative alcohols.

constants of alcohol using cyclohexane as reference are also shown in Table I. The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines and do not include an estimate of the error in the reference rate constants.

Rate constants determined in this experiment for the reactions of OH radicals with alcohols were compared with the previously reported data in Table I. In general, the present results are in good agreement with most previous studies to within experimental error. For *n*-propyl alcohol, the value reported by Campbell et al. [14] was about 35% lower than the others. As for isopropyl alcohol, the rate constant obtained by Lloyd et al. [16] was about 25% higher than others. Regarding the reaction rate constants of OH with *n*-butyl alcohol and *tert*-butyl alcohol, the results of Campbell et al. [14] for *n*-butyl alcohol and Saunders et al. [18] for *tert*-butyl alcohol are slightly lower than others. The data for *n*-pentyl alcohol obtained in this work are more than 13% greater than that of Wallington and Kurylo [11] and Nelson et al. [3] who performed the experiment by relative method, but are in fair agreement with that of Nelson et al. [3] using a PR-KS (pulse radiolysis kinetic spectroscopy) method. For isopentyl alcohol, there was only one previous value of $13.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Saunders et al. [18], which agrees very well with the values obtained in this work. Isobutyl alcohol has been measured for the first time. In the case of isobutyl alcohol, *n*-pentyl alcohol, and isopentyl alcohol, for which fewer rate constants are available in the literature, the deviation of the rate constants for each of the three compounds using two different references was less than 9%.

Cl Rate Constants

Rate constants for Cl atoms with alcohols have been measured using the relative method in previous studies [3]. However, the database for the reactions of Cl

with alcohols is still scarce. In the present work, the rate constants for Cl atoms with selected alcohols were studied using propane and cyclohexane as the reference hydrocarbons. Mixtures of the alcohols and reference hydrocarbons in the Teflon chamber were photochemically stable under our experimental conditions for nearly 2 h. After turning off the fluorescent lamps, and introducing Cl_2 into the chamber, the alcohols as well as the reference hydrocarbons were also stable in the dark for nearly 2 h. The experiments were carried out by irradiating the mixtures of alcohol/cyclohexane or propane/ Cl_2 /air under the light of fluorescent lamps. The initial concentrations were alcohol, 30–40 ppm; reference hydrocarbon, about 20 ppm; and Cl_2 , 40–50 ppm.

Figures 4 and 5 show plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([propane]_0/[propane]_t)$ while Figs. 6 and 7 show plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([cyclohexane]_0/[cyclohexane]_t)$ for the reactions of representative alcohols with Cl. On the basis of the rate constants of the reactions between Cl atoms with propane ($k = 1.31 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K) [21] and cyclohexane ($k = 3.07 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K) [22], the rate constants for the reactions of Cl atoms with the representative alcohols were calculated. Good agreement was obtained from the comparison between our values and those in the literature (as shown in Table II). The present work provides the first rate constants for the reactions of Cl with isobutyl alcohol and isopentyl alcohol. The rate coefficients of each alcohol based on different references agreed with each other to within $\pm 4\%$.

DISCUSSION

The data in Table I indicate that the rate constants for the reaction of OH radical with straight chain alcohols

Figure 4 Plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([propane]_0/[propane]_t)$ for the reaction of Cl with representative alcohols.

Figure 5 Plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([propane]_0/[propane]_t)$ for the reaction of Cl with representative alcohols.

increase almost linearly with the alkyl chain length from ethyl alcohol to *n*-pentyl alcohol. The larger rate constants for the reactions of OH radicals with the alcohols than with corresponding alkanes [22] obviously show the activating effect of the OH group. Nelson et al. [3] pointed out that the activating effect of the OH group could extend over about 4 carbon atoms for the OH radical reaction with straight chain alcohols, and that the CH_2 groups at the β -, γ -, and δ -positions in these molecules appear to show similar reactivity at about $2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Azad and Andino [24] have made an investigation of the OH radical initiated photooxidation of *n*-propyl alcohol with giving the product yields of 0.719 and 0.184 for propionaldehyde and acetaldehyde, respectively. Considering the *n*-propyl alcohol mechanisms initiated by OH radical [24] and the overall rate coefficient of $5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [7], the rate constants for OH radical attack at α - CH_2 , β - CH_2 , and γ - CH_3 can be estimated as 3.95×10^{-12} , 1.01×10^{-12} , and $0.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Obviously, the estimated rate constant for the OH radical attack at β - CH_2 is much less than that assumed by Nelson et al. [3]. This

Figure 6 Plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([cyclohexane]_0/[cyclohexane]_t)$ for the reaction of Cl with representative alcohols.

Figure 7 Plots of $\ln([alcohol]_0/[alcohol]_t)$ vs. $\ln([cyclohexane]_0/[cyclohexane]_t)$ for the reaction of Cl with representative alcohols.

inconsistency may imply that the OH group has small or even negligible activating effect at the CH_2 groups other than α - CH_2 for the reactions of OH radical with alcohols. Therefore, further mechanistic experiments about long straight chain alcohols would be interesting to test this assumption.

Table II Rate Constants for Cl with Alcohols at $\sim 295 \text{ K}$ Compared with Literature Data

Molecule	T (K)	K^a ($10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Reference ^b
Ethyl alcohol	295	8.45 ± 0.91	[23]
	298	10.1 ± 0.55	[3]
	295	10.3 ± 0.4	This work I
	295	9.6 ± 0.7	This work II
<i>n</i> -Propyl alcohol	295	14.4 ± 1.2	[23]
	298	14.9 ± 0.7	[3]
	295	15.3 ± 1.3	This work I
	295	14.7 ± 1.1	This work II
Isopropyl alcohol	298	8.40 ± 0.35	[3]
	295	7.35 ± 0.37	This work I
	295	8.27 ± 0.74	This work
<i>n</i> -Butyl alcohol	298	20.4 ± 1.4	[3]
	295	21.1 ± 1.1	This work I
	295	22.3 ± 1.0	This work II
Isobutyl alcohol	292	18.2 ± 0.4	This work I
	295	19.6 ± 1.1	This work II
<i>tert</i> -Butyl alcohol	295	3.26 ± 0.19	[23]
	295	3.15 ± 0.24	This work I
	295	3.41 ± 0.25	This work II
<i>n</i> -Pentyl alcohol	298	25.1 ± 1.3	[3]
	295	25.7 ± 2.5	This work I
	295	25.8 ± 1.2	This work II
Isopentyl alcohol	295	23.7 ± 0.7	This work I
	295	23.5 ± 0.9	This work II

^a Quoted errors represent 2σ from a least-squares analysis.

^b This work I, propane as the reference; This work II, cyclohexane as the reference.

For Cl atom reactions, it is interesting to note that the rate constants of straight chain alcohols are very similar to the corresponding alkanes [22], except ethyl alcohol. This may be due to such a high electron affinity of Cl that the H-abstraction is sufficiently facile. On the basis of the kinetics and mechanisms of the reaction of Cl atoms with *n*-propane and *n*-butane measured by Tyndall et al. [25], average values of 7.6×10^{-11} and 3.1×10^{-11} cm³ molecule⁻¹ s⁻¹ can be derived for the Cl attack at per-CH₂ and per-CH₃ group in alkanes. Cheema et al. [26] have carried out a quantitative analysis for the reaction of Cl atoms with *n*-propyl alcohol, and they estimated values of 8.7×10^{-11} , 4.7×10^{-11} , and 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹ for the Cl attack at α -CH₂, β -CH₂, and γ -CH₃ group, respectively. The activities of β -CH₂ and γ -CH₃ groups in *n*-C₃H₇OH towards Cl atom attack are clearly lower compared with the CH₂ and CH₃ groups in alkanes. We thus concur with Cheema that the presence of an OH group seems to lower the rate constants for the Cl attack at β -CH₂ and raise the rate constant at α -CH₂.

Comparison between the rate constants for the reactions of OH radical and Cl atoms with alcohols, the rate constants of Cl atoms with alcohols are 1–2 orders of magnitude higher than that of the corresponding reactions of OH radicals. In free troposphere, the removal of alcohols is dominated by the reactions with OH radicals because the concentration of OH radical is much higher than atomic Cl, whereas in marine boundary layer and coastal urban areas, maximum predicted Cl atom levels may reach a peak of 1.3×10^5 atoms cm⁻³ shortly after sunrise [6], and so the role of Cl atoms is also of great importance in these areas.

BIBLIOGRAPHY

- Atkinson, R. *J Phys Chem Ref Data* 1994, Monograph 2, 1–216.
- Tuazon, E. C.; Carter, W. P. L.; Aschmann, S. M.; Atkinson, R. *Int J Chem Kinet* 1991, 23, 1003–1015.
- Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielson, O. J. *Int J Chem Kinet* 1990, 22, 1111–1126.
- Stutz, J.; Ezell, M. J.; Ezell, A. A.; Finlayson-Pitts, B. J. *J Phys Chem A* 1998, 102, 8510–8519.
- Finlayson-Pitts, B. J.; Keoshian, C. J.; Buehler, B.; Eaell, A. A. *Int J Chem Kinet* 1999, 31, 491–499.
- Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastringe, I. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* 1998, 394, 353–355.
- Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F. J.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J Phys Chem Data* 1999, 28, 191–203.
- Cox, R. A.; Goldstone, A. In *Proceedings from the 2nd European Symposium on the Physico-Chemical Behavior of Atmospheric Pollutants*, D. Riedel Publishing Co., Holland, 1982, pp. 112–119.
- Greenhill, P. G.; O'Grady, B. V. *Aust J Chem* 1986, 39, 1775–1787.
- Kerr, J. A.; Stocker, D. W. *J Atmos Chem* 1986, 4, 253–262.
- Wallington, T. J.; Kurylo, M. J. *Int J Chem Kinet* 1987, 19, 1015–1023.
- Hess, W. P.; Tully, F. P. *J Phys Chem* 1989, 93, 1944–1947.
- Overend, R.; Paraskevopoulos, G. *J Phys Chem* 1978, 82, 1329–1333.
- Compbell, I. M.; McLaughlin, D. F.; Handy, B. J. *Chem Phys Lett* 1976, 38, 362–364.
- Yujing, M.; Mellouki, A. *Chem Phys Lett* 2001, 333, 63–68.
- Lloyd, A. C.; Darnall, K. R.; Winer, A. M.; Pitts, J. N., Jr. *Chem Phys Lett* 1976, 42, 205–208.
- Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Environ Sci Technol* 1988, 22, 842–844.
- Saunders, S. M.; Baulch, D. L.; Cooke, K. M.; Pilling, M. J.; Smurthwaite, P. I. *Int J Chem Kinet* 1994, 26, 113–130.
- Teton, S.; Mellouki, A.; Le Bras, G. *Int J Chem Kinet* 1996, 28, 291–297.
- Atkinson, R. *Chem Rev* 1985, 85, 69–201.
- Mellouki, A. *J Chim Phys* 1998, 95, 513–522.
- Aschmann, S. M.; Atkinson, R. *Int J Chem Kinet* 1995, 27, 613–622.
- Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C. H.; Japar, S. M. *Int J Chem Kinet* 1988, 20, 867–875.
- Azad, K.; Andino, J. M. *Int J Chem Kinet* 1999, 31, 810–818.
- Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. *Int J Chem Kinet* 1997, 29, 43–45.
- Cheema, S. A.; Holbrook, K. A.; Oldershaw, G. A.; Walker, R. W. *Int J Chem Kinet* 2002, 34, 110–121.