Kinetics and Mechanism Associated with the Reactions of Hydroxyl Radicals and of Chlorine Atoms with 1-Propanol under Near-Tropospheric Conditions Between 273 and 343 K

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ABSTRACT: Rate constants for the reactions of OH radicals and Cl atoms with 1-propanol (1-C₃H₇OH) have been determined over the temperature range 273–343 K by the use of a relative rate technique. The value of $k(Cl + 1-C_3H_7OH) = (1.69 \pm 0.19) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K and shows a small increase of 10% between 273 and 342 K. The value of $k(OH + 1-C_3H_7OH)$ increases by 14% between 273 and 343 K with a value of $(5.50 \pm 0.55) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K, and further when combined with a single independent experimentally determined value at 753 K gives $k(OH + 1-C_3H_7OH) = 4.69 \times 10^{-17}$ T^{1.8} exp(422/T) cm³ molecule⁻¹ s⁻¹, which fits each data point to better than 2%. Two well-established structure–activity relationships for H abstraction by OH radicals give accurate predictions of the rate constant for OH + 1-C₃H₇OH, provided the β -CH₂ group is given an increased reactivity of a factor of about 2 over that for the structurally equivalent CH₂ group in alkanes at 298 K.

Correspondence to: Ray Walker; e-mail: r.w.walker@hull.ac.uk. © 2001 John Wiley & Sons, Inc. DOI 10.1002/kin.10027 A quantitative product analysis was carried out at 298 K for the Cl-initiated photooxidation of $1-C_3H_7OH$, using both FTIR and gas chromatography. HCHO, CH₃CHO, and C₂H₅CHO were the only major organic primary products observed, although HCOOH was found in much smaller amounts as a secondary product. A key characteristic of the analysis was that the initial values of the product ratio [CH₃CHO]/[C₂H₅CHO] were effectively constant for NO pressures between 0.15 and 0.3 Torr, but fell by about 35% as the pressure fell to 0.0375 Torr. From a detailed consideration of the mechanism for the oxidation, it is suggested that C₂H₅CHO, CH₃CHO (+HCHO), and 3 molecules of HCHO are formed uniquely from CH₃CH₂CHOH, CH₃CHCH₂OH, and CH₂CH₂CH₂OH radicals, respectively. On this basis, use of the product yields gives the branching ratios of 56, 30, and 14% for Cl atom reaction at the α -, β -, and γ - C—H positions in 1-C₃H₇OH at 298 K. Given the very low temperature coefficients involved, little change will occur over tropospheric temperature ranges. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 110–121, 2002

INTRODUCTION

The most important oxidizing process in any oxidation, either in combustion or in a photochemical smog, is OH + fuel molecule. A detailed knowledge of the reactions of OH radicals in both atmospheric chemistry [1] and combustion [2] is vital for the modelling of intermediate and product species, and for improvements in the level of tropospheric pollution and in combustion efficiency, which of course are linked. Normally Cl atoms are unimportant in combustion, except as a source of pollution, but may be key species in atmospheric chemistry, particularly in marine environments where [Cl]/[OH] could be a factor of 1000 higher than usual [3]. There is indisputable evidence of the importance of Cl atom reactions with alkanes (and related compounds) in the lower troposphere during springtime in the Arctic [4]. In the stratosphere, reaction with smaller alkanes, particularly methane, provides a sink for Cl atoms and a consequent reduction in the catalytic removal of ozone [5]. Further, Cl atoms are frequently used in laboratory studies to initiate oxidation and other processes, so that reliable kinetic data are required [6]. Rigorous modelling of tropospheric oxidation requires not only the overall rate constants but also reliable information on first, the branching ratios for attack at the various sites in the molecule, and second the subsequent reactions of the radicals formed.

In addition to their use as solvents, alcohols have found increasing use in clean- and lean-burning combustion engines. As a consequence, the C_1-C_4 alcohols in particular are found in relatively high concentration as pollutants in the troposphere. They show a number of interesting kinetic and mechanistic effects. For example, Wallington et al. [7] have shown that in the reaction of OH radicals with linear alcohols, not only is the reactivity of the α -CH₂ considerably enhanced over that observed for the group in alkanes at 298 K, but the increased activity extends certainly to the β -CH₂ and perhaps as far as the γ -CH₂. Hess and Tully [8] have shown in a series of elegant experiments that β -hydroxyalkyl radicals tend to decompose above about 500 K, particularly in the absence of oxygen, so that measurements of the rate constants for OH + alcohol, which monitor the OH concentration will underestimate their values, as illustrated below for OH + ethanol.

$$OH + C_2H_5OH \rightarrow CH_2CH_2OH + H_2O$$

 $CH_2CH_2OH \rightarrow CH_2 = CH_2 + OH$

Reactions of α -hydroxyalkyl radicals formed from ethanol and 2-butanol under tropospheric conditions [9] and of α - and β -hydroxyalkyls formed from 2propanol [6] have been studied in detail, as well as by Atkinson and coworkers, as discussed in his review article [10].

Relatively little information is available on the tropospheric chemistry of 1-propanol. Rate constants for its reaction with OH radicals and Cl atoms are only available at 298 K, and no study has been made of the oxidation products. In the present work a relative rate method is used to determine the kinetics of both Cl atoms and OH radicals with 1-propanol over the temperature range 273–343 K, and FTIR and gas chromatographic analysis are used to monitor the products of the Cl-initiated photooxidation of 1-propanol, from which the branching ratios for Cl attack on the compound may be calculated.

It should be noted that Walker and coworkers have obtained a value for $k(OH + 1-C_3H_7OH)$ at 753 K from their well-established method, which involves the addition of $1-C_3H_7OH$ to mixtures of $H_2 + O_2$ (Walker, R. W., unpublished work); the value will be discussed later.

EXPERIMENTAL

A static high-vacuum Pyrex apparatus with PTFE taps was used to prepare reaction mixtures. The system was evacuated by an oil diffusion pump (Edwards Diffstak Model 63), backed by a two-stage oil rotary pump. The degree of evacuation (about 10^{-5} Torr) was measured with a Penning Gauge, capable of measurement down to 10^{-7} Torr. Two Baratron Capacitance Manometers of differing ranges 0–10 and 0–1000 Torr were used to measure the various pressures of reactants with a precision of about 0.1%.

A relative rate technique, similar to that employed by Aschmann and Atkinson [11], was employed to study the kinetics of the $Cl + 1-C_3H_7OH$ and $OH + 1-C_3H_7OH$ reactions. OH radicals were generated by the photolysis of methylnitrite in the presence of O₂, NO, $1-C_3H_7OH$, 2,3-dimethylbutane (the reference compound for the OH radical kinetics) and added N₂ to a total pressure of 700 Torr.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
 (1)

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
 (2)

$$HO_2 + NO \rightarrow NO_2 + OH$$
 (3)

Once prepared [12], the methylnitrite was subjected to repeated freeze-pump-thaw treatment and stored under vacuum at 77 K.

Cl atoms were generated by the photolysis of Cl_2 in the presence of O_2 , NO, 1-C₃H₇OH, C_2H_6 (the reference gas), and added N₂ to a total pressure of 700 Torr.

In the presence of Cl atoms and OH radicals, $1-C_3H_7OH$ and the reference compounds are removed via reactions (4)–(7).

$$Cl + 1 - C_3 H_7 OH \rightarrow products$$
 (4)

 $Cl + C_2H_6 \rightarrow products$ (5)

$$OH + 1 - C_3 H_7 OH \rightarrow products$$
 (6)

$$OH + (CH_3)_2 CHCH(CH_3)_2 \rightarrow products$$
 (7)

Tests showed that no reaction occurred in the dark even at times well in excess of those used in the kinetic experiments, so that providing 1-C₃H₇OH and the two reference compounds (ref) are consumed solely through reaction with Cl atoms and OH radicals the value of the relative rate constant may be calculated at any temperature by use of Eq. (I). The subscripts 0 and *t* represent the concentrations at zero time and reaction time *t*, and k_x/k_{ref} is equal to k_4/k_5 and k_6/k_7 for the Cl atom and OH radical experiments, respectively. Plots of ln([C₃H₇OH]₀/[C₃H₇OH]_t) against ln([ref]₀/[ref]_t) should give straight lines through the origin with slopes equal to the value of the appropriate rate constant ratio.

$$\ln([C_3H_7OH]_0/[C_3H_7OH]_t)$$

= $(k_x/k_{ref})\ln([ref]_0/[ref]_t)$ (I)

The kinetic experiments were carried out in a 250 cm³ cylindrical Pyrex vessel irradiated by a 75 W Xenon-Arc ultraviolet lamp fitted with an ellipsoid reflector. Experiments with cylindrical vessels of volume varying between 100 and 1000 cm³ gave effectively identical results, and this observation together with the very high level of reproducibility observed confirm the absence of surface effects. The reaction vessel was placed in a thermostatted water bath fitted with a quartz window for transmission purposes. The concentrations of 1-C₃H₇OH and of the reference compounds were analyzed before and after irradiation by use of a Carlo-Erba gas chromatograph coupled to a Shimadzu Chromatopac 3-RA integrator and data processor. Successful quantitative analysis for both sets of kinetic experiments was achieved on a $1.5 \text{ m} \times 1/8 \text{ in}$. stainless steel Porapak column, which was also used for analysis of products. Considerable care was taken to avoid interference by products and excellent resolution was fine-tuned by small changes in the operating temperature. A 1.0 m \times 1/8 in. stainless steel Porapak QS column was used to analyze for acids.

In-situ FTIR analysis of the Cl-initiated photooxidation of 1-C₃H₇OH was carried out in a 16 l cylindrical quartz cell, 92 cm in length and 15 cm in diameter, by use of a Nicolet Magna-IR Spectrometer Model 550 system. The quartz vessel was fitted with a three-mirror, gold-coated, White reflection system for multiple passes of the infra-red beam, and equipped with a LaserMark system that greatly simplified cell alignment. The beam traveled a pathlength of 28 m through the sample in 36 passes. Eight fluorescent blacklights (Sylvania F20T12/350 BL 20 W/GTE Products Corporation, USA) were used as the light source and were covered with 1-mm thick aluminum sheeting to prevent scattering of the ultraviolet radiation to the surroundings. The spectrum was taken at better than 0.5 cm⁻¹ resolution. Absorption coefficients were measured for 1-C3H7OH and its anticipated products by direct measurements over a range of pressure. The products identified and analyzed quantitatively by FTIR are given in Table I together with their spectral characteristics. Other minor products identified, but not measured, were HNO₃

 Table I
 Compounds Determined by FTIR Analysis^a

Compound	Wave number (cm^{-1})
1-C ₃ H ₇ OH	3680.6
C ₂ H ₅ CHO	849.0
CH ₃ CHO	2701.4
НСНО	2780
НСООН	1105

^aWave numbers determined directly by use of pure materials.

(3551.4 cm⁻¹), HO₂NO₂(1304 cm⁻¹), and N₂O₅ (1245 cm⁻¹). Attempts were made to detect possible products such as propionic acid, peroxyacetylnitrate(PAN), and peroxypropionylnitrate(PPN) by comparing their spectra with the spectrum from the irradiated mixture, but no specific characteristic peaks were found. It is concluded that these products were formed below the detectable level.

Prior to irradiation experiments in both vessels, the gas mixtures were allowed to stand in the dark for 15 min to attain reaction temperature and to ensure full mixing.

RESULTS

Kinetics of the Cl and OH Reactions with 1-Propanol

Figures 1 and 2 show plots based on the application of Eq. (I) for Cl + 1-C₃H₇OH and OH + 1-C₃H₇OH, respectively, at two temperatures. Similar plots with good straight lines, all passing effectively through the origin, with the point 0,0 not treated as an experimental value, are obtained at all the temperatures used. The values of the relative rate constants k_4/k_5 and k_6/k_7 , obtained directly from the gradients of the plots are given in Table II.

The kinetics of reaction (5) have been investigated extensively at low temperatures by both absolute and relative rate methods, and summarized in a recent review by Atkinson [13]. Results from the plethora of investigations at 298 ± 2 K suggest that k_5 is known to better than 10% at this temperature. Several investigators have recorded a small temperature coefficient between 250 and 400 K, with activation energies varying between (500 \pm 365) [14] and (1120 \pm 170) kJ



Figure 1 Relative rate plots for the reaction $Cl + 1-C_3H_7OH$ (a) 298 K; (b) 332 K.



Figure 2 Relative rate plots for the reaction $OH + 1-C_3H_7OH$ (a) 273 K; (b) 343 K.

mol⁻¹ [15]. Pilgrim et al. [15] have demonstrated significant curvature in the variation of ln k_5 with reciprocal temperature above 600 K, but consider that Arrhenius expressions may be used below. Atkinson [13] has recommended $k_5 = 8.3 \times 10^{-11} \exp(-100/T) \text{ cm}^3$ molecule⁻¹ s⁻¹ for use between 220 and 600 K, and this expression will be adopted here.

The absolute values of k_4 are given in Table II. It should be noted that as the values of k_4/k_5 are independent of temperature and can be determined accurately, the temperature coefficients of (4) and (5) are effectively equal at least between 270 and 350 K. There are only two other independent values of k_4 , both obtained by the relative rate method. Wallington et al. [16] give $k_4 = (1.49 \pm 0.12) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at}$ 295 K, relative to $k_5 = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson's recommendation [13], adopted here), and Nelson et al. [17] give $k_4 = (1.49 \pm 0.07) \times 10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹ at 298 K, relative to k(Cl + c-hexane) $= 3.11 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, recommended by Atkinson [13]. In Arrhenius form, the present results give $k_4 = (2.68 \pm 0.20) \times 10^{-10} \exp[(-128 \pm 20)/T]$ cm^3 molecule⁻¹ s⁻¹ between 273 and 343 K. The error limits refer to $\pm 2\sigma$ from least squares analysis of the rate constants.

The kinetics of reaction (7) have been studied by a number of groups and, following a least squares analysis of the data, Atkinson [10] recommends $k_7 = 1.24 \times 10^{-17} T^2 \exp(494/T)$ cm³ molecule⁻¹ s⁻¹ between 250 and 1200 K. Use of this expression with the present values of k_6/k_7 gives the absolute values of k_6 listed in Table II. They show a small increase with temperature, and over the range 273–343 K give $k_6 = (9.8 \pm 0.45) \times 10^{-12} \exp[(-172 \pm 210)/T]$ cm³ molecule⁻¹ s⁻¹ No other Arrhenius parameters are available for reaction (6), but Table III compares the values obtained at room

T (K)	k4/k5	$10^{10}k_4$ (cm ³ molecule ⁻¹ s ⁻¹)	k ₆ /k ₇	$10^{12}k_6$ (cm ³ molecule ⁻¹ s ⁻¹)
273	2.88 ± 0.03	1.65 ± 0.18	0.930 ± 0.034	5.25 ± 0.56
298	2.86 ± 0.03	1.69 ± 0.19	0.952 ± 0.028	5.50 ± 0.55
313	_	_	0.962 ± 0.054	5.66 ± 0.74
314	2.91 ± 0.05	1.75 ± 0.21	_	
323	2.93 ± 0.03	1.78 ± 0.20	_	
332	2.91 ± 0.03	1.79 ± 0.20	_	
342	2.90 ± 0.05	1.81 ± 0.21	_	
343	—	—	0.969 ± 0.026	5.97 ± 0.77

 Table II
 Summary of Rate Constants for the Reactions of Cl and OH with 1-C3H7OH

temperature. Atkinson et al. [13] have remarked that the low value obtained by Campbell et al. [18] may have been caused by undetected problems with the experimental technique. The agreement with the other results is excellent when it is considered that both absolute and relative rate techniques were employed, the latter with three different reference compounds. The low range of values $(5.33-5.64) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ places considerable confidence in the value used for k_7 , particularly as Atkinson [10] quotes a possible uncertainty of about 25% at 298 K.

Products of the Cl-Initiated Oxidation of 1-Propanol

Figure 3 shows the FTIR concentration–time profiles for the mixture containing $1-C_3H_7OH = 0.095$, chlorine = 0.020, NO = 0.0300, O₂ = 140, and N₂ = 560 Torr at 298 K. The characteristic frequencies

Table III Kinetic Data Available for the Reaction of OH Radicals with $1-C_3H_7OH$

T (K)	$10^{12}k_6$ (cm ³ molecule ⁻¹ s ⁻¹)	Technique	Reference
298	5.50 ± 0.55	R.R. ^a	This work
292	3.9 ± 0.7	$R.R.^{b}$	[18]
296	5.33 ± 0.54	FP-RA ^c	[19]
296	5.34 ± 0.39	$FP-RF^{d}$	[20]
298	5.29 ± 0.43	R.R. ^{<i>e</i>}	[17]
298	$5.64\pm~0.48$	$PR-KS^{f}$	[17]

^{*a*}Relative to $k(OH + 2,3\text{-dimethylbutane}) = 5.78 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ [10].

^bRelative to $k(OH + 1\text{-butane}) = 2.36 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [13].

^cAbsolute by flash photolysis-resonance absorbance.

^dAbsolute by flash photolysis-resonance fluorescence.

^eRelative to $k(OH + c\text{-hexane}) = 7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10].

^f Absolute by pulse radiolysis-kinetic spectroscopy.

used to identify $1-C_3H_7OH$ and the major initial products, propanal, ethanal, methanal, and formic acid are given in Table I. It is clear that formic acid is only formed in any significant quantity as a secondary product. Other products identified at very low concentrations were HNO₃, HO₂NO₂, and N₂O₅. Other possible products such as propionic acid, PAN, and PPN, if formed, were at concentrations below the detectable limit. Table IV summarizes the analysis data, which demonstrate a good carbon recovery balance and lend strong support to the view that no major product from $1-C_3H_7OH$ remains undetected over the period of analysis.

The products were also investigated by gas chromatography using the mixture containing $1-C_3H_7OH =$ 0.5, chlorine = 0.10, O₂ = 140, and N₂ = 560 Torr, and five different pressures of NO between 0.0375 and 0.300 Torr. Only two major product peaks were observed, and identified as propanal and ethanal. Previous experience had shown that methanal could not be detected under the conditions used. Small peaks, each



Figure 3 Plot of product pressures determined by FTIR against irradiation time at 298 K 1-C₃H₇OH = 0.095, chlorine = 0.020, NO = 0.0300, O₂ = 140, N₂ = 560 Torr ×, 1-C₃H₇OH (right side scale); •, HCHO; \circ , C₂H₅CHO; Δ , CH₃CHO \Box , HCOOH (×10).

Irradiat time (s)	10 ² C ₃ H ₇ OH (Torr)	10 ² C ₂ H ₅ CHO (Torr)	10 ² HCHO (Torr)	10 ³ CH ₃ CHO (Torr)	10 ⁴ HCOOH (Torr)	%C recovered
0	9.65	0	0	0	0	_
279	8.98	0.56	0.41	0.57	0	109
417	8.26	1.08	1.02	2.19	0.10	112
553	7.93	1.32	1.34	2.86	0.65	113
691	7.61	1.44	1.50	4.02	1.31	107
828	7.37	1.54	1.62	4.89	2.35	106
965	7.12	1.65	1.71	5.28	3.40	102
1102	6.96	1.73	1.77	5.63	4.05	101
1239	6.80	1.80	1.77	5.92	5.23	99
1376	6.56	1.86	1.77	6.68	6.41	95
1514	6.48	1.91	1.83	6.88	7.59	95

Table IV Product Analysis by FTIR for the Cl-Initiated Photooxidation of 1-C₃H₇OH^a

^{*a*} Mixture composition: $1-C_3H_7OH = 0.0965$, $Cl_2 = 0.020$, NO = 0.300, $O_2 = 140$, $N_2 = 560$ Torr at 298 K.

corresponding to likely yields of less than 1% were observed at 0.67, 0.93, 3.45, 13.75, and 38.8 min were not identified. Specific analysis for methanol, ethanol, oxirane (ethylene oxide), hydroxyacetone, and propionic acid indicated that if formed they were below the detectable level.

Table V summarizes the absolute yields of propanal and ethanal at 298 K at different extents of reaction for the five different pressures of NO used, together with the product ratio $[CH_3CHO]/[C_2H_5CHO]$. The product ratios show a modest increase with extent of irradiation due to consumption of the two products at differing rates. Reasonably good extrapolation to zero consumption may be made, and the initial values of $[CH_3CHO]/[C_2H_5CHO]$ are plotted against the pressure of NO used in Fig. 4. The value of the ratio is constant for pressures of NO between 0.150 and 0.300 Torr, but falls significantly at lower pressures. There is, however, clear consistency between the values obtained by gas chromatography and FTIR, where the NO pressure was 0.0300 Torr.

DISCUSSION

Cl-Initiated Oxidation of 1-Propanol

The mechanism of the photooxidation of $1-C_3H_7OH$ may be elucidated by considering the product profile, which shows that propanal, ethanal, and methanal are the only major initial products derived from the alcohol. Based on independent studies of the photooxidation of ethanol [9] and 2-propanol [6], Schemes 1–3 show the proposed mechanism for the oxidation of the radicals formed following H atom abstraction by Cl atoms at the α , β , and γ positions in $1-C_3H_7OH$. Abstraction from the OH group is considered too slow to compete at the low temperatures used here [10,13]. It is proposed that propanal is formed from the 1-hydroxy-1-propyl radical (Scheme 1) either directly by reaction (8) with O_2 or indirectly through the formation of the 1-hydroxy-1-propoxy radical produced by the reaction of NO with 1-hydroxy-1-propylperoxy radicals (10). Steps (11) and (12) are precluded because of

Table VYields of Ethanal and Propanal by GasChromatography from the Cl-Initiated Photooxidationof $1-C_3H_7OH$

	1-C ₃ H ₇ OH	CH.CHO	C. H. CHO	
NO (Torr)	(%)	(%)	(%)	$[C_2H_5CHO]/$
0.0375	9.6	2.28	6.7	0.34
0.0375	15.4	3.68	10.2	0.36
0.0375	16.1	2.80	7.8	0.36
0.0375	25.2	5.74	13.8	0.41
0.0375	30.1	4.06	11.9	0.39
0.0750	11.8	3.15	6.8	0.46
0.0750	24.5	5.34	12.1	0.44
0.0750	25.9	5.87	12.2	0.48
0.0750	29.6	6.12	13.1	0.47
0.0750	33.7	7.02	14.3	0.49
0.150	20.6	5.86	10.0	0.59
0.150	27.1	7.35	12.6	0.58
0.150	30.9	8.55	13.3	0.64
0.150	41.1	8.52	13.3	0.65
0.225	13.6	4.32	8.1	0.53
0.225	18.3	6.05	10.5	0.58
0.225	29.0	8.90	14.1	0.63
0.225	30.9	10.8	15.0	0.72
0.225	47.0	11.6	15.8	0.73
0.300	13.9	4.15	7.9	0.54
0.300	23.6	6.60	11.3	0.58
0.300	36.6	8.41	13.5	0.62
0.300	42.1	9.66	14.6	0.66
0.300	48.3	11.5	15.9	0.72



Figure 4 Plot of the initial values of $[CH_3CHO]/[C_2H_5CHO]$ against the pressure of NO at 298 K. o, gas chromatography; $1-C_3H_7OH = 0.5$, chlorine = 0.10, $O_2 = 140$, $N_2 = 560$ Torr. ×, FTIR (product ratio at 15% consumption of $1-C_3H_7OH$); see Fig 3 for mixture composition.

the absence of formic and propionic acids in the initial products, and as (11) and (12) are about 115 and 290 kJ mol⁻¹, respectively, less endothermic than (13) it may be concluded that propanal is formed from 1-hydroxy-1-propyl radicals almost exclusively in reaction (8) in accordance with previous studies of the behavior of α -hydroxyalkyl radicals under tropospheric conditions [9]. Further, the absence of formic acid in the initial products precludes any formation of ethanal in reaction (14), because C₂H₅ radicals will not be formed.

It is structurally likely that ethanal is formed as an initial product from the 1-hydroxy-2-propyl radical, as



Scheme 1 Attack at the α -CH₂ position in 1-C₃H₇OH.



HCHO + HO₂ HCHO + HO₂ Scheme 2 Attack at the β -CH₂ position in 1-C₃H₇OH.

shown in Scheme 2. There is no fast direct reaction with O_2 analogous to reaction (8) for the 1-hydroxy-1-propyl radical, and formation of the peroxy species followed by reaction with NO to give the 1-hydroxy-2-propoxy radical is the obvious path. Reaction (18) is ruled out by the demonstrated absence of hydroxyacetone. Analysis shows that if formed at all, the yield does not exceed 1% of the total product. Formation of ethanal, with the same mole% of methanal, through reaction (17) is therefore the sole fate of the 1-hydroxy-2-propoxy radical. This conclusion is fully consistent with the observations made by Niki et al. [21] who demonstrated nearly 100% formation of both ethanal and methanal from the 1-hydroxy-2-propoxy radical



during the OH-initiated photooxidation of propene at 298 K.

Scheme 3 shows the proposed initial oxidation chemistry of the 1-hydroxy-3-propyl radical formed by Cl attack at the γ -position in 1-C₃H₇OH. There is no fast direct reaction with O₂, any formation of CH₂=CHCH₂OH + HO₂ having a rate constant no higher than 1×10^{-15} cm³ molecule⁻¹ s⁻¹ compared with a value of approximately 1×10^{-12} cm³ molecule⁻¹ s⁻¹ for the formation of 1-hydroxy-3propylperoxy radicals. Following rapid reaction with NO in (23), the resulting 1-hydroxy-3-propoxy radical, given the absence of 3-hydroxypropanal in the products, follows the sequence (24) and (26) to give three methanal molecules.

Given the apparent simplicity of the mechanism in the early stages of reaction, namely that 1-hydroxy-1-propyl, 1-hydroxy-2-propyl, and 1-hydrox-3-propyl radicals react uniquely to give propanal, ethanal (+methanal), and three methanal molecules, respectively, it is clearly possible to determine the branching ratios for Cl attack on 1-C₃H₇OH at 298 K. The sole inconsistency surrounds the observation shown in Fig. 4 that the initial product ratio [CH₃CHO]/[C₂H₅CHO] falls at the lower NO pressures used. Reference to the consumption of 1-C₃H₇OH shows that the effect is due to the falling yield of ethanal. Although consistent with the steady yield of propanal, which is formed in the direct reaction of 1-hydroxy-1-propyl radicals with O₂, the obvious possibility that as the NO pressure falls the otherwise inert peroxy radicals undergo self-reaction is difficult to accept unless the rate constant for the reaction of 1-hydroxy-2-propylperoxy radicals with NO is a factor of about 10³ lower than the normal value of about $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [22]. At 298 K, with the mixtures used, the rate of formation of ethanal is approximately 1.0×10^{-4} Torr s⁻¹ so that with NO = 0.03 Torr and $k_{15} = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (= 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (= 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ s$ 10^5 Torr⁻¹ s⁻¹), then [1-hydroxy-2-propylperoxy] = 1.0×10^{-8} Torr, and the rate of reaction (15) is 3×10^{6} faster than that of reaction (27), even with k_{27} as high as the unlikely value [10] of 1×10^{-11} cm³ molecule⁻¹ s⁻¹. Only if k_{15} is reduced by a factor of 10³ and the high value of k_{27} retained would the two reactions become competitive. There is no evidence in the literature that these two conditions can be met [10,13,23]. Further, simple calculations based on kinetic theory [24] show that removal of the peroxy radicals at the surface, even if efficient, is far too slow to compete with reaction (15). Further conjecture is premature in the absence of additional experimental information, particularly given the potential complexity of the chemistry involved. For the determination of the branching ratios for C1 + $1-C_3H_7OH$, it will be assumed that Schemes 1-3 give a true account of the oxidation chemistry and that the steady values of $[CH_3CHO]/[C_2H_5CHO]$ at high NO pressures are appropriate.

$$CH_3CH(OO)CH_2OH + RO_2 \rightarrow products$$
 (27)

Following the conclusion reached earlier that Cl attack at the α -, β -, and γ - positions leads uniquely to propanal, to ethanal and methanal, and to 3 molecules of methanal, respectively, then from the experimental observations $[CH_3CHO]/[C_2H_5CHO] = 0.54$ and $([HCHO] - [CH_3CHO])/[C_2H_5CHO] = 0.76, 56, 30,$ and 14% reaction occurs at the three positions, respectively at 298 K. Arising from the very low temperature coefficients involved, little change in these percentages will occur between 240 and 400 K. Taking the mean of the value determined here and those available in the literature, $k_4 = 1.55 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, giving $k_{4\alpha} = 8.7 \times 10^{-11}$, $k_{4\beta} = 4.7 \times 10^{-11}$, and $k_{4\gamma}$ $= 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. No other values are available in the literature, but Ohta et al. [6] from a similar analysis of the Cl-initiated oxidation of 2propanol suggest that 85% of the Cl attack occurs at the α -position and 15% at the β -methyl groups at 298 K so that $k_{28\alpha}/k_{28\beta} = 5.7$. Atkinson [13] recommends $k_{28} =$ $8.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which gives $k_{28\alpha} =$ 7.1×10^{-11} and $k_{28\beta} = 1.3 \times 10^{-11}$ cm³ molecule⁻¹ s^{-1} from Ohta's data.

$$\begin{split} \text{Cl} + (\text{CH}_3)_2\text{CHOH} &\rightarrow (\text{CH}_3)_2\text{COH} + \text{HCl} \quad (28\alpha) \\ \text{Cl} + (\text{CH}_3)_2\text{CHOH} &\rightarrow \text{CH}_3\text{C}(\text{CH}_2)\text{CHOH} + \text{HCl} \\ \end{split}$$

Reactions (4γ) and (28β) both involve attack on a CH₃ group, but on a per C–H bond basis, the rate constants differ by a factor of 3.5 in favor of (4γ) . Although when discussing the relative rate of attack at the two positions in 2-propanol, Ohta et al. [6] argue that differences in the C–H bond dissociation energies, and therefore in the activation energies could be the explanation, there is no evidence [13] other than for Cl + methane that the activation energies themselves could exceed 1 kJ mol⁻¹, and hence the factor of 3.5 is likely to arise from some other cause.

The value of $k_{4\beta} = 4.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 298 K, may be compared with the values given by Nelson et al. [17] for the increase in the overall rate constants for the homologous series of linear alkanols from methanol to octanol, 5.3×10^{-11} , 4.8×10^{-11} , 5.5×10^{-11} , 4.7×10^{-11} , 4.4×10^{-11} , 5.4×10^{-11} , 4.5×10^{-11} , the mean increment for the insertion of a CH₂ group being 4.9×10^{-11} cm³ molecule⁻¹ s⁻¹. The consistency implies that a value of $(4.8 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ may be taken for Cl attack at a CH₂ group other than at the α -position to the OH group.

The increases in the rate constant for Cl + alkanes from ethane to octane due to the insertion of CH₂ groups are significantly larger, (7.8, 8.1, 6.2, 6, 5, 7) 1×10^{-11} cm³ molecule⁻¹ s⁻¹ [10] at 298 K, which is reflected in Atkinson's structure-activity relationships (SAR) where a value of 7.3×10^{-11} is given for a CH₂ group adjacent to a methyl group and 5.8×10^{-11} cm³ molecule⁻¹ s⁻¹ with two CH₂ groups as neighbors. The presence of an OH group therefore appears to lower the rate constant for attack at the β -CH₂ in linear alcohols. The CH₃ group may be taken as isolated from the OH group in 1-C₃H₇OH, and application of Atkinson's SAR method predicts a value of $k_{4\gamma} = 2.7 \times$ 10^{-11} in satisfactory agreement with the experimental value of 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹ obtained in the present study.

The extremely low or zero temperature coefficient arises because k_4/k_5 (which may be measured very accurately) is independent of temperature between 273 and 343 K and the value of k_5 increases by only about 10%. In Arrhenius terms, a positive value for E_4 is not anticipated if $E_{4\gamma} = E_5$, and $E_{4\alpha}$ and $E_{4\beta}$ are less than $E_{4\gamma}$ and likely from the sparse information available in the literature [10] to be zero or even negative. The value of $E(Cl + CH_3OH) = 0$ between 248 and 573 K [25], $E_5 \sim 1.0 \text{ kJ mol}^{-1}$, although Pilgrim and coworkers [15] have demonstrated significant non-Arrhenius behavior above 600 K, and $E(Cl + C_3H_8) = E(Cl + C_3H_8)$ $1-C_4H_{10}$ = 0 between 250 and 600 K [15,25]. Only the reaction $Cl + CH_4$ shows a marked temperature coefficent, with an activation energy of about 12 kJ mol^{-1} [10] between 250 and 400 K and a pronounced non-Arrhenius curvature at higher temperatures [15].

Table VI shows the rate constants for the reactions of O [26], OH and Cl [13] with methane, ethane, ethanol, and $1-C_3H_7OH$ at 298 K, and demonstrates a novel feature in the case of Cl atoms. The relative rates show a

monotonic increase from methane to 1-C₃H₇OH as expected from considerations of bond energy, activation energy, and the number of C-H bonds available for reaction. However, while the relative rate changes by 78 and 39 for O and OH, respectively, from methane to ethane, the change for Cl atoms is 590, which would correspond to an activation energy difference of about 16 kJ mol $^{-1}$ which, within experimental tolerance, is equal to the difference in the C-H bond energies in the two alkanes. This characteristic would not be inconsistent with a change in mechanism between methane and ethane, with that for the former having a "normal" transition state for H abstraction. Although the polarity in the OH group in alcohols could provide an alternative reaction path, whereby the transition state involves the initial formation of a partial bond between Cl and the slightly positive H atom in the OH group followed by the formation of a loose ring involving an H atom attached to a C atom, it is not easy to suggest a plausible difference in the cases of methane and ethane.

It should be noted in regard to the temperature coefficent of reaction (4), that an assumption of equal A factors per C-H bond gives from the present results $E_{4\gamma} - E_{4\alpha} = 4.4 \text{ kJ mol}^{-1}$ and $E_{4\beta} - E_{4\alpha} = 1.53 \text{ kJ}$ mol⁻¹. With $E_{4\alpha}$ taken as zero, the very small variation of k_4 with temperature is predicted precisely. However, it is difficult to accept an activation energy of 4.4 kJ mol^{-1} for the reaction of Cl atoms at the CH₃ group in 1-C₃H₇OH when $E(Cl + C_2H_6)$ is approximately 1 kJ mol⁻¹, a value which has been confirmed in several studies [13]. Alternatively, although Cl attack at the OH group in alcohols is usually regarded as negligible at 298 K [13], there is little confirmation and should this path contribute 5% to the overall value of k_4 at 273 K with an activation energy of 5 kJ mol⁻¹, then with $E_{4\alpha} = E_{4\beta} = 0$ and $E_{4\gamma} = 0.85$ kJ mol⁻¹ the value of k_4 would increase by 5% between 273 and 343 K compared with the experimental value of 10%. No decision can be reached and further discussion on the temperature variation of k_4 and the values of the specific A factors and activation energies is premature

Table VI Comparison of Rate Constants^a for Reactions of Cl Atoms, O Atoms, and OH Radicals

RH	$k(O + RH)^b$	Relative	$k(OH + RH)^c$	Relative	$k(Cl + RH)^c$	Relative
CH ₄	$5.0 imes 10^{-18}$	1	6.4×10^{-15}	1	$9.9 imes 10^{-14}$	1
C_2H_6	$3.9 \times 10^{-16^{d}}$	78	$2.5 imes 10^{-13}$	39	$5.9 imes 10^{-11}$	595
C ₂ H ₅ OH	5.4×10^{-14}	10800	3.2×10^{-12}	500	9.0×10^{-11}	910
1-C ₃ H ₇ OH	$(5-10) \times 10^{-14}$	$(1-2) \times 10^3$	5.5×10^{-12}	860	1.5×10^{-10}	1520

^{*a*}Units are in cm^3 molecule⁻¹ s⁻¹.

^bHerron [26].

^cAtkinson et al. [13].

^dMean of values recommended by Herron [26] and Baulch et al. [27].

until more information is available on the effect of temperature over a wider range, and on Cl atom reactions in general.

OH-Initiated Oxidation of 1-Propanol

In the absence of a product study no direct information is available on the relative importance of OH attack at the different H atom sites in $1-C_3H_7OH$. However, the SAR method is more reliable for OH radicals because of the greater wealth of data available, and this approach may be used to determine the branching ratios.

Cohen [28] has used semiempirical transition state theory to calculate rate constants for H abstraction from alkanes by OH radicals, and Bott and Cohen [29] have given the values $9.3 \times 10^{-18} T^{1.8} \exp(275/T)$, $5.0 \times 10^{-19} T^{2.2}$ exp(860/T), and $5.6 \times 10^{-18} T^{1.9}$ $\exp(-255/T)$ cm³ molecule⁻¹ s⁻¹ for abstraction at the methyl, methylene and hydroxyl groups in ethanol, respectively. With these values used for $k_{6\alpha}$, $k_{6\gamma}$, and $k_{6\text{OH}}$, together with $k_{6\beta} = 4.45 \times 10^{-17} T^2 \exp(300/T)$, recommended by Cohen [27] for the CH₂ group in butane, the value of k_6 may be predicted over a range of temperature. However, accepting the validity of using Cohen's value for $OH + \alpha - CH_2$ in ethanal for that in 1-C₃H₇OH, unless the importance of attack at the β -CH₂ group in 1-C₃H₇OH is raised there is a fall in the predicted value of k_6 of 5% between 273 and 313 K. Although the observed rise of about 8% may not in itself be significant, the difference between the observed and predicted temperature coefficients should be considered so. Further, there is a considerable body of evidence to suggest that the β -CH₂ group and even the γ -CH₂ group, in addition to the α -CH₂, are activated by the presence of the OH group [10,13]. Figure 5 shows the predicted values of k_6 using Bott and Cohen's SAR data, but with value of $k_{6\beta}$ $= 4.45 \times 10^{-17} T^2 \exp(506/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$ which corresponds to a factor of 2 increase in the value at 298 K over that given above for a CH₂ group in butane.

Atkinson [10] has formulated an SAR based on the function $AT^2 \exp(B/T)$ for use with alkanes. Here $k = 2.9 \times 10^{-13}$ cm³ molecule ⁻¹ s⁻¹ at 298 K is taken for attack at a β -CH₃ group following the study of OH + 2-methyl-2-propanol by Baulch and coworkers [30], and combined with $k = 8.1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 600 K obtained by Hess and Tully [8] for attack at the CH₃ group in ethanol. Combination of these values gives in the above form $k(OH + \beta$ -CH₃) = $1.56 \times 10^{-18}T^2 \exp(219/T)$ cm³ molecule⁻¹ s⁻¹. Reaction of OH radicals at the OH group has been assigned the same parameters, but with the A factor



FIGURE 5 Plot of $k(OH + 1-C_3H_7OH)$ against reciprocal temperature. \bigcirc , present work; \times (Walker, R. W. unpublished work); —— based on Cohen's structure–activity relationship (SAR) [28, 29]; ------ based on Atkinson's SAR [13].

reduced by a factor of 3. At low temperatures, little error will be introduced into the total rate constant, but extrapolation to high temperatures may underpredict the amount of reaction at the OH group if the temperature coefficient has been underestimated. From the value of $k(OH + C_2H_5OH) = 6.18 \times 10^{-18}T^2 \exp(532/T)$ cm³ molecule⁻¹ s⁻¹ between 293 and 600 K quoted by Atkinson [13], based on the results of Hess and Tully [8], then by subtraction and after allowance for nearneighbour effects [10], $k = 4.60 \times 10^{-18} \exp(638/T)$ cm^3 molecule⁻¹ s⁻¹ for the reaction of OH radicals at the α -CH₂ position in 1-C₃H₇OH. As shown by studies of OH + ethanol [8] and OH + 2-methy-2-propanol [29], the reactivity of β -CH₃ groups in alkanols is increased by a factor of 2 over that for CH₃ groups in alkanes [10], and this factor is applied for $OH + \beta - CH_2$ in 1-C₃H₇OH compared with the reaction of OH with CH_2 in alkanes [10], giving $k(OH + CH_3CH_2CH_2OH)$ $= 4.50 \times 10^{-18} T^2 \exp(491/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ Figure 5 shows the predicted relationship between k_6 and temperature using the parameters given above for the four sites of attack in 1-C₃H₇OH. A small increase in rate constant between 273 and 343 K is predicted by both the Cohen and the Atkinson SAR approaches. It must be emphasized that the kinetic parameters obtained independently have not been modified to achieve agreement, although clearly an almost exact fit in both cases could be found by very small changes in the individual parameters. More importantly, as shown in Fig. 5, both SAR methods predict values close to the experimental value of $k_6 = 1.23 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at 753 K, obtained by Walker (unpublished manuscript) from studies of the addition of 1-C₃H₇OH to mixtures of $H_2 + O_2$ mixtures. It is also of interest to note that similar studies give

Group	Based on Atkinson SAR	Based on Cohen SAR
CH ₃ CH ₂ CH ₂ - <u>OH</u> CH ₂ CH ₂ -CH ₂ -OH	$5.2 \times 10^{-19} T^2 \exp(219/T)^b$ 4.6 × 10 ⁻¹⁸ T ² exp(638/T)	$5.65 \times 10^{-18} T^{1.9} \exp(-255/T)$ 6.6 × 10 ⁻¹⁹ T ^{2.2} exp(800/T)
$CH_3-\underline{CH_2}-CH_2OH$	$4.5 \times 10^{-18} T^2 \exp(491/T)$	$4.45 \times 10^{-19} T^2 \exp(506/T)^c$
CH ₃ -CH ₂ CH ₂ OH	$4.5 \times 10^{-18} T^2 \exp(-258/T)^d$	$2.75 \times 10^{-17} T^{1.8} \exp(-480/T)$

Table VII SAR Group Parameters^{*a*} used for the reaction $OH + 1-C_3H_7OH$

^aUnits are in cm³ molecule⁻¹ s⁻¹.

^bTaken as one-third of attack at CH₃ group in CH₃CHO by reduction in the A factor.

^cCohen's value for a CH₂ group in butane, increased by a factor of 2 at 298 K through the exponential term [28].

^dAtkinson's value for CH₃ group attached to a CH₂ group in alkanes [10].

 $k(OH + C_2H_5OH) = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 753 K in excellent agreement with a value of 7.1 × 10⁻¹² calculated from Atkinson's recommended expression given above. The consonance of the two is of particular interest because, as shown by Hess and Tully [8] and discussed by Bott and Cohen [28], methods which measure the rate constant for OH + alkanols by measurement of the OH concentration underestimate the value because attack at the β-position gives radicals which readily undergo decomposition above 500 K to generate OH radicals, as shown below for ethanol and 1-C₃H₇OH.

 $\label{eq:CH2CH2OH} \begin{array}{l} CH_2CH_2OH \rightarrow C_2H_4 + OH \\ \\ CH_3CHCH_2OH \rightarrow C_3H_6 + OH \end{array}$

The expression $k_6 = 4.69 \times 10^{-17} T^{1.8} \exp(422/T)$ cm³ molecule⁻¹ s⁻¹, which fits the available experimental data to better than 2%, is recommended for use between 250 and 1200 K, with uncertainties in the rate constant of 15% at 298, rising to 25% at 753 and 75% at 1200 K.

The SAR relationships based on both the Atkinson and the Cohen approaches and used here are summarized in Table VII. It is pertinent to point out, as emphasized by one of the referees, that the transition state theory calculations of Cohen do not properly take account of "tunneling," so that use of his parameters (Table VII) for k_6 should not be used for extrapolation noticeably below 273 K.

Tropospheric Lifetimes

The calculated tropospheric lifetime of $1-C_3H_7OH$ with respect to OH radicals is 2.7 days at 298 K, for an OH concentration of 7.7×10^5 radical cm⁻³ [31], and with respect to Cl atoms is approximately 70 days for a Cl concentration of 1×10^4 atom cm⁻³ [3].

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