

# Kinetic Studies of OH Reactions with *Iso*-Propyl, *Iso*-Butyl, *Sec*-Butyl, and *Tert*-Butyl Acetate

STÉPHANE LE CALVÉ, GEORGES LE BRAS, ABDELWAHID MELLOUKI

Laboratoire de Combustion et Systèmes Réactifs, CNRS and Université d'Orléans, 45071 Orléans Cedex 2, France

Received 14 November 1996; accepted 27 January 1997

**ABSTRACT:** The temperature dependence of the rate coefficients for the OH radical reactions with *iso*-propyl acetate ( $k_1$ ), *iso*-butyl acetate ( $k_2$ ), *sec*-butyl acetate ( $k_3$ ), and *tert*-butyl acetate ( $k_4$ ) have been determined over the temperature range 253–372 K. The Arrhenius expressions obtained are:  $k_1 = (0.30 \pm 0.03) \times 10^{-12} \exp[(770 \pm 52)/T]$ ;  $k_2 = (1.09 \pm 0.14) \times 10^{-12} \exp[(534 \pm 79)/T]$ ;  $k_3 = (0.73 \pm 0.08) \times 10^{-12} \exp[(640 \pm 62)/T]$ ; and  $k_4 = (2.22 \pm 0.34) \times 10^{-12} \exp[-(395 \pm 92)/T]$  (in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). At room temperature, the rate constants obtained (in units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) were as follows: *iso*-propyl acetate ( $3.77 \pm 0.29$ ); *iso*-butyl acetate ( $6.33 \pm 0.52$ ); *sec*-butyl acetate ( $6.04 \pm 0.58$ ); and *tert*-butyl acetate ( $0.56 \pm 0.05$ ). Our results are compared with the previous determinations and discussed in terms of structure-activity relationships. © 1997 John Wiley & Sons, Inc. *Int J Chem Kinet* **29**: 683–688, 1997.

## INTRODUCTION

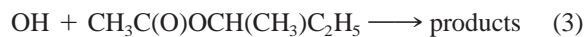
Acetates are emitted into the atmosphere by various anthropogenic or natural sources. They are used to a large extent in industry, particularly as solvents, and in the manufacturing of perfumes and flavorings; they are also produced in nature through vegetation [1]. A substantial proportion of these compounds could escape then into the atmosphere where they are available for photochemical transformation. Another source of acetates is the tropospheric degradation of oxygenated compounds, especially ethers. For example, *iso*-propyl acetate is produced from *iso*-propyl ether which is used as an additive in unleaded gasoline to increase the octane rating [2].

The main tropospheric fate of the acetates is the reaction with OH radicals, since photolysis [3] reaction with  $\text{NO}_3$  radicals [4] and reaction with  $\text{O}_3$  [5] are slow processes, thus negligible in the atmospheric degradation of these VOCs. The atmospheric oxidation of these oxygenated compounds initiated by the OH radicals could contribute to the formation of ozone and other components of the photochemical smog in urban areas. To assess the impact of the acetates on air quality, accurate kinetic and mechanistic data concerning their reactivity toward OH radicals are needed.

In this article, absolute rate constants  $k_1$ – $k_4$  are reported for reaction of the OH radical with four acetates: *iso*-propyl acetate, *iso*-butyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate, in the temperature range 253–372 K:



Correspondence to: A. Mellouki  
Contract grant Sponsor: French Ministry of Environment  
Contract grant Sponsor: European Commission  
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The few existing data available in the literature for reactions (1), (3), and (4) have been obtained only at room temperature. We report herein the first kinetic data for the reaction (2) and the first temperature dependence kinetic data for the four reactions (1), (2), (3), and (4).

## EXPERIMENTAL

The pulsed laser photolysis–laser induced fluorescence (PLP–LIF) apparatus and procedures used to measure  $k_1$ – $k_4$  have been described in previous publications from this laboratory [6,7]. Therefore, only information necessary to understand this work is presented here.

Hydroxyl radicals were generated by photolysis of  $\text{H}_2\text{O}_2$  at  $\lambda = 248$  nm (KrF excimer laser) and their concentration monitored using laser induced fluorescence. A Nd:YAG pumped frequency doubled dye laser was used to excite the OH radical at 282 nm. Fluorescence from the OH radical was detected by a photomultiplier, fitted with a 309 nm narrow bandpass filter, positioned below the reaction volume and coaxial with the gas flow. Both the photolysis and the probe lasers were operated at a repetition rate of 10 Hz and the probe laser triggered at variable delay times after the photolysis pulse. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically the fluorescence signal from 10 to 15 different delay times from 100 probe laser shots were averaged to generate OH concentration-time profiles over at least three lifetimes. Acetate/ $\text{H}_2\text{O}_2$  mixtures in helium diluent were flowed vertically through the cell mutually orthogonal to the photolysis and the probe laser beams. The intersection of the laser beams at the center of the cell defines the observation volume. The reaction mixture was slowly flowed through the cell, so that each photolysis/probe sequence interrogates a fresh gas mixture and reaction products did not build up in the cell.

The helium carrier gas (UHP certified to >99.9995% (Alphagas)) was used without purification. The 50 wt. %  $\text{H}_2\text{O}_2$  solution obtained from Pro-labo, was concentrated by bubbling helium through the solution to remove water for several days prior to use, and constantly during the course of the experiments. It was admitted into the reaction cell by passing a small flow of helium through a glass bubbler con-

taining  $\text{H}_2\text{O}_2$ . Isopropyl acetate ( $\geq 99.5\%$ ) and *iso*-butyl acetate (99%) were from Fluka, *sec*-butyl acetate and *tert*-butyl acetate ( $\geq 99\%$ ) were from Aldrich. These compounds were further purified by repeated freeze, pump, and thaw cycles and fractional distillation before use.

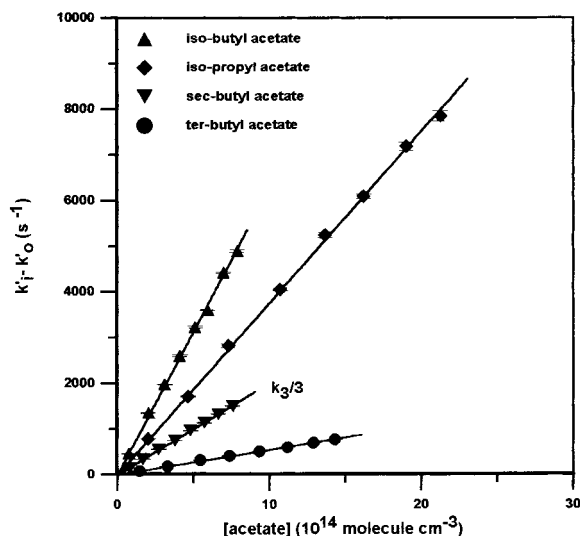
For the kinetic measurements, the studied acetate was premixed with helium in a 10 L glass light-tight bulb to form (1–4)% mixture at a total pressure of  $\approx 800$  torr. All the gases flowed into the reactor through Teflon tubing. The gas mixture containing the acetate, the photolytic precursor ( $\text{H}_2\text{O}_2$ ), and the bath gas (approximately 100–300 torr of helium) were flowed through the cell with a linear velocity ranging between 5 and 20  $\text{cm s}^{-1}$ . The concentrations of reactants and the bath gas were calculated from their mass flow rates, the temperature, and the pressure in the reaction cell. All flow rates were measured with mass flowmeters calibrated by measuring the rate of pressure increase in a known volume. The pressure in the cell was measured with a capacitance manometer connected at the cell entrance.

## RESULTS AND DISCUSSION

Reactions (1–4) were studied under pseudo-first-order in OH; the OH concentration was much lower than that of acetate. The acetate concentration ranges were (in  $10^{14}$  molecule  $\text{cm}^{-3}$ ) (1.24–36.30), (0.54–17.26), (0.44–16.27), and (1.10–35.05) for *iso*-propyl acetate, *iso*-butyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate, respectively. The initial OH concentration,  $[\text{OH}]_0$ , was always less than  $2 \times 10^{11}$  molecule  $\text{cm}^{-3}$  [6]. Under these conditions, the OH concentration time profile followed the pseudo-first-order rate law:

$$[\text{OH}]_t = [\text{OH}]_0 e^{-k't} \quad \text{where } k' = k_i[X_i] + k'_0$$

$X_i$  refers to the acetate in reaction  $i$  ( $i = 1-4$ ) and  $k_i$  is the rate coefficient for the reaction of OH with the acetate ( $i$ ). The decay rate,  $k'_0$ , is the first-order OH decay rate in the absence of the acetate. The value of  $k'_0$  is essentially the sum of the reaction rate of OH with its precursor ( $\text{H}_2\text{O}_2$ ), and the diffusion rate of OH out of the detection zone. Plots of  $(k' - k'_0)$  vs. the acetate concentration obtained at room temperature for the different acetates are shown in Figure 1. In all cases the data show excellent linearity and  $k_i$  values were derived from the least-squares fit of the straight lines. The quoted errors for  $k_i$  determined in this work include  $2\sigma$  from the least-squares analysis and the es-



**Figure 1** Plots of  $(k'_i - k'_0)$  vs acetate concentration at room temperature ( $i = 1-4$ ). The lines represent the linear least-squares fitting.

timated systematic error 5% (due to uncertainties in measured concentrations).

All the compounds being studied were pure to better than 99%, the loss of OH radicals by reaction with impurities in the gas mixtures is expected to be insignificant.

The four acetates were analyzed in our laboratory using GC/MS. In the case of *tert*-butyl acetate where 1% of reactive impurities could affect the measured rate constants, the analysis indicated that the 1% impurities is due mainly to *tert*-butyl alcohol which have an OH reaction rate constant around  $1 \times 10^{-12}$  [8]. That implies a very small error ( $\leq 1\%$ ) due to impurities on the measured rate constants for the reaction of OH with *tert*-butyl acetate. Possible contributions to the measured rate constants from secondary reactions of OH with the products of reactions (1)–(4) were significantly reduced by using high range ( $10^2$ – $10^4$ ), of [acetate]/[OH] ratios which did not show any difference in measured  $k_i$  values. Also rate constants were shown to be independent of variations in the gas-flow velocity through the reactor or changes in the total pressure of the system. The investigated acetates do not absorb at 248 nm, the wavelength at which  $\text{H}_2\text{O}_2$  was photolyzed to generate OH radicals [3]. Hence, reaction of OH with photofragments of the acetates cannot contribute to OH loss since no photofragments were produced. As expected, variations in the photolysis fluence had no effect on the determined rate coefficients.

The measured rate coefficients for the reactions of OH with the acetates determined over the temperature range 253–372 K are listed in Table I. They are also

**Table I** Reactions OH + *iso*-Propyl Acetate (1), OH + *iso*-Butyl Acetate (2), OH + *sec*-Butyl Acetate (3), OH + *tert*-Butyl Acetate (4): Summary of Experimental Conditions and Measured  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$

T (K)	[ <i>iso</i> -propyl acetate]		[ <i>iso</i> -butyl acetate]		[ <i>sec</i> -butyl acetate]		[ <i>tert</i> -butyl acetate]	
	( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_1 \pm 2\sigma)^b$	( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_2 \pm 2\sigma)^b$	( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_3 \pm 2\sigma)^b$	( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_4 \pm 2\sigma)^b$
253	1.58 – 12.94	$6.31 \pm 0.30$					1.71 – 17.06	$4.87 \pm 0.34$
253	1.96 – 20.89	$6.46 \pm 0.06$					1.44 – 12.94	$5.07 \pm 0.21^c$
263	1.87 – 19.74	$5.56 \pm 0.07$	0.81 – 8.42	$8.91 \pm 0.31$	0.81 – 8.89	$8.58 \pm 0.26$	1.45 – 16.45	$5.00 \pm 0.21$
263			0.76 – 8.86	$8.72 \pm 0.22$	0.78 – 8.49	$8.58 \pm 0.14$		
273	2.38 – 24.07	$4.77 \pm 0.14$	0.79 – 8.14	$8.03 \pm 0.24$	0.84 – 8.27	$7.83 \pm 0.30$	1.57 – 14.55	$5.26 \pm 0.32$
283	2.37 – 22.91	$4.34 \pm 0.08$	0.81 – 7.23	$7.02 \pm 0.24$	0.86 – 7.97	$7.17 \pm 0.09$	1.68 – 16.63	$5.66 \pm 0.15$
298	2.00 – 21.25	$3.74 \pm 0.10$	0.75 – 7.89	$6.27 \pm 0.20$	0.67 – 6.79	$6.12 \pm 0.28$	1.55 – 16.06	$5.84 \pm 0.26$
298	1.49 – 16.17	$3.80 \pm 0.07$	0.77 – 7.85	$6.23 \pm 0.11$	0.77 – 7.58	$6.02 \pm 0.10$	1.63 – 16.36	$5.39 \pm 0.26$
298	1.52 – 16.22	$3.85 \pm 0.10^c$	0.76 – 7.88	$6.50 \pm 0.19$	0.74 – 7.65	$5.99 \pm 0.18$	1.20 – 12.89	$5.83 \pm 0.21$
298	2.88 – 31.08	$3.75 \pm 0.12^d$	0.79 – 7.67	$6.41 \pm 0.26^c$	0.79 – 7.37	$6.27 \pm 0.17^c$	1.45 – 14.32	$5.41 \pm 0.13$
298	3.21 – 36.30	$3.79 \pm 0.11^e$	1.28 – 13.49	$6.53 \pm 0.20^d$	1.43 – 14.05	$5.97 \pm 0.16^d$	2.82 – 28.30	$5.84 \pm 0.14^d$
298			1.47 – 17.26	$6.17 \pm 0.25^e$	1.52 – 16.27	$6.01 \pm 0.20^e$	3.24 – 35.05	$5.35 \pm 0.16^e$
298							2.86 – 28.92	$5.57 \pm 0.20^e$
313	1.40 – 15.74	$3.42 \pm 0.13$	0.71 – 7.40	$5.91 \pm 0.10$	0.70 – 7.38	$5.46 \pm 0.13$	1.18 – 12.50	$6.18 \pm 0.33$
333	1.72 – 19.79	$2.92 \pm 0.05$	0.68 – 6.17	$5.06 \pm 0.19$	0.76 – 7.07	$4.94 \pm 0.21$	1.37 – 14.25	$6.44 \pm 0.34$
333							1.18 – 12.05	$6.65 \pm 0.21$
353	1.75 – 18.92	$2.64 \pm 0.06$	0.68 – 6.53	$5.03 \pm 0.11$	0.44 – 5.28	$4.56 \pm 0.13$	1.21 – 10.85	$7.71 \pm 0.38$
372	1.73 – 15.73	$2.49 \pm 0.08$	0.54 – 4.69	$5.00 \pm 0.19$	0.76 – 6.36	$4.34 \pm 0.16$	1.10 – 10.86	$8.29 \pm 0.35$
372	1.24 – 13.13	$2.53 \pm 0.09$	0.64 – 6.40	$4.76 \pm 0.12$	0.59 – 6.07	$4.27 \pm 0.14$	1.39 – 12.80	$8.11 \pm 0.38$

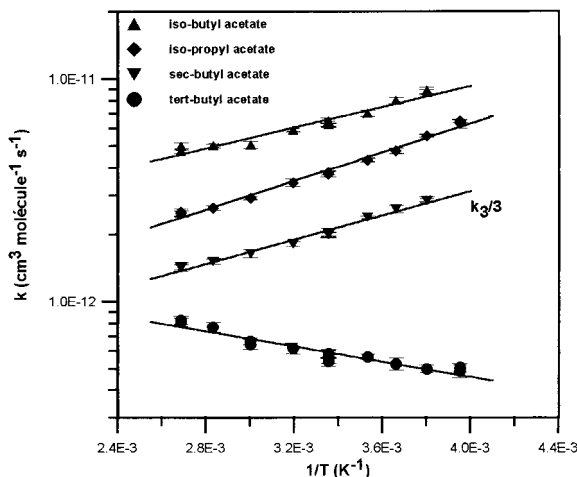
<sup>a</sup> Units of molecule  $\text{cm}^{-3}$ .

<sup>b</sup> Units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

<sup>c</sup> Variation of the photolysis laser fluence (decrease by a factor of 3).

<sup>d</sup> Variation of flow velocity (decrease by a factor of 3).

<sup>e</sup> Experiments carried out at 300 Torr.



**Figure 2** Plots of  $k_1$  to  $k_4$  vs.  $1/T$ . The solid lines represent the two parameter least-squares fits to the individual data points for each acetate. The error bars of the individual point are  $2\sigma$  and do not include estimated systematic errors.

shown in Figure 2 in the conventional Arrhenius form ( $k = Ae^{-E_a/RT}$ ). The plots show a slight negative temperature dependence of the rate constant for the all acetates, except for *tert*-butyl acetate, for which a slight positive temperature dependence was observed. The Arrhenius parameters for the OH reactions with these acetates are given in Table II where the obtained data are summarized along with those from previous studies.

### Comparison with Previous Results

While we report the first determination for  $k_2$ , a few data have been published so far for  $k_1$ ,  $k_3$ , and  $k_4$  at room temperature (see Table II). For  $k_1$ , comparison can be made with the results of Kerr and Stocker [9] and Wallington et al. [10] who used the relative rate

and flash photolysis-resonance fluorescence techniques, respectively. Excellent agreement is observed between our determination and that of Wallington et al. These data and the measurement of Kerr and Stocker also agree within the given uncertainty ranges even if this later is around 20% lower. There is also a good agreement between our  $k_3$  value and those from Winer et al. [11] and Wallington et al. [10]. For  $k_4$ , the value obtained at room temperature in the present work is 27% higher than the relative rate determination reported by Smith et al. [12]. To our knowledge there have been no temperature dependence studies of  $k_1$ – $k_4$  which we can compare our results with.

### Trends in the OH + Acetate Reaction Rate Constants

In a previous work from this laboratory [13], we confirmed that OH radical reacts by H-atom abstraction predominantly with the alkoxy end of the acetates rather than with the acetyl end, and comparison of the room temperature rate coefficients shows an increase in the reactivity from methyl acetate to *n*-pentyl acetate. The observed reactivity agreed well with reactivity calculated from the structure-activity relationship (SAR) of Atkinson based on group reactivity [14]. This SAR has been applied to the rate constant calculation for reactions of OH with organic molecules including acetates. In the updated SAR data base [14] the substituent factors of the  $-C(O)OR$  and  $-OC(O)R$  ester groups were calculated to be  $F(-C(O)OR) = 0.74$  and  $F(-OC(O)R) = 1.6$  at 298 K. Using these values, the SAR gives the following calculated rate constants which compare well for  $k_1$ ,  $k_3$ , and  $k_4$  with the experimental ones (in brackets)  $k_1 = 3.55$  (3.77),  $k_3 = 5.41$  (6.04),  $k_4 = 0.60$  (0.56), while for  $k_2$  there is some discrepancy  $k_2 = 4.67$

**Table II** Comparison of OH Reaction Rate Coefficients with Previous Work

Molecule	$T$ , K	$k$ , $10^{-12}$ $\text{cm}^3$ molecule $^{-1}$ s $^{-1a}$	$A$ , $10^{-12}$ $\text{cm}^3$ molecule $^{-1}$ s $^{-1a,b}$	$E/R$ , K $^{a,b}$	$T$ range, K	Technique $^c$	Ref.	
$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$	303	$3.08 \pm 0.84$	–	–	–	RR	[9]	
	296	$3.72 \pm 0.29$	–	–	–	FP–RF	[10]	
	298	$3.77 \pm 0.29$	$0.30 \pm 0.03$	$-(770 \pm 52)$	253–372	LP–LIF	This work	
$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)_2$	298	$6.33 \pm 0.52$	$1.09 \pm 0.14$	$-(534 \pm 79)$	263–372	LP–LIF	This work	
	$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{C}_2\text{H}_5$	305	$5.4 \pm 1.1$	–	–	–	RR	[11]
		296	$5.65 \pm 0.59$	–	–	–	FP–RF	[10]
$\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$	298	$6.04 \pm 0.58$	$0.73 \pm 0.08$	$-(640 \pm 62)$	263–372	LP–LIF	This work	
	298	$0.44 \pm 0.04$	–	–	–	RR	[12]	
	298	$0.56 \pm 0.05$	$2.22 \pm 0.34$	$(395 \pm 92)$	253–372	LP–LIF	This work	

<sup>a</sup> Errors are those given by the authors.

<sup>b</sup> For our data, the uncertainties for the Arrhenius parameters  $A$  and  $E/R$  are given by  $\Delta A = 2A \sigma_{\ln A}$  and  $\Delta E/R = 2\sigma_{E/R}$  for the Arrhenius forms.

<sup>c</sup> Key to techniques: LP–LIF, Laser Photolysis–Laser Induced Fluorescence; FP–RF, Flash Photolysis–Resonance Fluorescence; and RR, Relative Rate.

(6.33), (in units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K). This discrepancy might indicate some limitation of the SAR method which, by definition, assumes that a substituent group influences the reactivity of only the  $\text{CH}_3$ ,  $\text{CH}_2$ , or  $\text{CH}$  group in  $\alpha$  position. An activating effect of the O atom of the alkoxy end extended to CH group in  $\beta$  position in the *iso*-butyl acetate molecule might significantly increase the calculated  $k_2$  value since H-atom abstraction occurs predominantly at the CH group ( $k(\text{CH}) = 0.5 k_2$  from the SAR calculation). Similar effect on the  $\text{CH}_2$  group in  $\beta$  position in the *sec*-butyl acetate molecule would also increase the calculated value of  $k_3$ , making it closer to the experimental value. The enhancement would be, however, less important considering the lower contribution of  $k(\text{CH}_2)$  to  $k_3$  than  $k(\text{CH})$  to  $k_2$  ( $k(\text{CH}_2) = 0.2 k_3$  from the SAR calculation).

The SAR calculated contribution of the different carbon groups to the overall rate constants are given below for the four studied acetates:

$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ (3%) (87%) ( $2 \times 5\%$ )	$k_1$
$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)_2$ (2%) (39%) (51%) ( $2 \times 4\%$ )	$k_2$
$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (2%) (71%) (3%) (21%) (3%)	$k_3$
$\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$ (16%) (3 $\times$ 28%)	$k_4$

As expected, these calculated contributions to the overall rate constants indicate that reactions mainly occur on secondary and/or tertiary carbon groups when the molecules contain such groups. Besides, the partial rate constant of the alkyl group in the alkoxy end of the acetates can be estimated by subtracting from the  $k_1$ – $k_4$  values obtained in this work the partial rate constant of the  $\text{CH}_3$  group in the acetyl end of the acetates. This later is taken as  $k(\text{CH}_3) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K, which is consistent with the SAR calculation ( $k(\text{CH}_3) = 1.01 \times 10^{-13}$  [14]), and half of the experimental rate constant value of the reaction  $\text{OH} + \text{acetone}$  ( $k(\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_3) = 2.19 \times 10^{-13}$ , recommended value from Atkinson [15], and  $(1.84 \pm 0.24) \times 10^{-13}$  recently obtained in our laboratory [16]).

The deduced partial rate constants for the *iso*-propyl, *iso*-butyl, *sec*-butyl, and *tert*-butyl groups of the corresponding acetates are, respectively: 3.67, 6.23, 5.94, and 0.46 (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and can be compared with alkanes and ethers. The corresponding values (in units of  $10^{-12} \text{ cm}^3$

$\text{molecule}^{-1} \text{ s}^{-1}$ ) for the same groups in (1) alkanes are, respectively: 3.00, 4.33, 4.43, and 0.53 [15]; (2) in ethers, they are, respectively: 5.1 [17], 13.0 [18], and 1.9 [8] (no data are available for ethers containing the *sec*-butyl group). The comparison of these values indicates that the reactivity of the alkyl groups in acetates is higher than in alkanes but lower than in ethers, which is indeed consistent with the SAR substituent factors in alkanes, acetates, and ethers:  $F(-\text{CH}_3) = 1$ ,  $F(-\text{CH}_2-) = F(-\text{CH}) = F(>\text{C}) = 1.23$ ,  $F(-\text{OC}(\text{O})\text{R}) = 1.6$ ,  $F(-\text{OR}) = 8.4$  [14].

### Temperature Dependence of the OH + Acetate Reaction Rate Constants

Except for  $k_4$ , which has a slight positive temperature dependence, the temperature coefficient of the other measured rate constants is negative and about the same ( $-500 \text{ K} \geq E/R \geq -800 \text{ K}$ ), within the temperature range studied (253–372 K). The rate coefficients obtained in this work on acetates and in previous ones on ethers and linear acetates, from our laboratory [7, 8, 13], show a slight positive temperature dependence for dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ), methyl *tert*-butyl ether ( $\text{CH}_3\text{OC}(\text{CH}_3)_3$ ), methyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ ), and *tert*-butyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$ ). These four molecules contain only methyl groups, thus confirming that H-atom abstraction from a  $\text{CH}_3$  group has a positive temperature dependence. In contrast, in compounds containing the more reactive  $-\text{CH}_2-$  or  $-\text{CH}-$  group, the OH reaction rate constants have negative temperature dependences. These temperature dependences may provide some support for formation of weakly bound complexes between OH radical and the acetates which can either decompose back to reactants or eliminate  $\text{H}_2\text{O}$ . However, direct bimolecular reactions may also show a negative temperature dependence if they have near zero activation energies and a negative temperature dependent preexponential factor.

The observed negative temperature dependence of the plots  $\ln k = f(1/T)$  of  $k_1$ ,  $k_2$ , and  $k_3$  fit well with a straight line in the temperature range studied (Fig. 1). However, the very slight curvature of the plots might suggest the existence of a positive temperature dependence of  $k$  at higher temperatures. Such changes in temperature dependences of  $k$  have been clearly observed in the same range of temperature as in the present study for the reactions of OH with methyl acetate and ethyl acetate [10,13]. This was interpreted by considering two different mechanisms: formation of a long-lived adduct with further  $\text{H}_2\text{O}$  elimination at low temperature, and direct H atom transfer at high temperature. This is not inconsistent with our obser-

variations. These two mechanisms could also exist for reactions of OH with *iso*-propyl, *iso*-butyl, and *sec*-butyl acetates but the OH-adduct suggested to be formed at low temperature would be more stable than the lighter OH-methyl acetate and OH-ethyl acetate adducts. Then, the addition mechanism would be predominant for reactions (1), (2), and (3) in the temperature range investigated. Further measurements at higher temperature are needed to check this hypothesis.

### Atmospheric Implication

Concerning the atmospheric implication, the rate constant data obtained in the present study contribute to better define the tropospheric lifetimes of the studied acetates which react predominantly with the OH radical. With a typical tropospheric OH concentration of  $1 \times 10^6$  molecule  $\text{cm}^{-3}$  the following tropospheric lifetimes ( $\tau = 1/k_r[\text{OH}]$ ) are calculated in days: 3.1, 1.8, 1.9, and 21 for *iso*-propyl acetate, *iso*-butyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate, respectively. In addition, the obtained rate constant data combined with structure activity relationship give semi-quantitative information on the initial attack sites of the acetate molecules, hence on peroxy radical intermediates and further oxidation products to be formed in the atmospheric degradation of the acetates.

French Ministry of Environment and European Commission for support.

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