

## Kinetic Studies of OH Reactions with a Series of Methyl Esters

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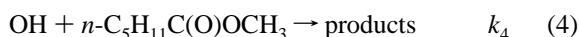
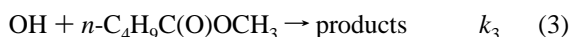
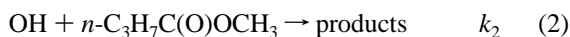
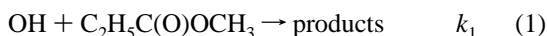
Absolute rate constants have been measured for the gas-phase reactions of hydroxyl radicals with a series of methyl esters: methyl propionate ( $k_1$ ), methyl butyrate ( $k_2$ ), methyl valerate ( $k_3$ ), and methyl caproate ( $k_4$ ). Experiments were carried out using the pulsed laser photolysis–laser induced fluorescence technique over the temperature range 253–372 K. The obtained kinetic data were used to derive the following Arrhenius expressions:  $k_1 = (1.45 \pm 0.42) \times 10^{-12} \exp[-(148 \pm 86)/T]$ ;  $k_2 = (0.96 \pm 0.29) \times 10^{-12} \exp[(380 \pm 91)/T]$ ;  $k_3 = (1.37 \pm 0.64) \times 10^{-12} \exp[(401 \pm 142)/T]$ ;  $k_4 = (2.46 \pm 1.04) \times 10^{-12} \exp[(326 \pm 130)/T]$  (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: methyl propionate ( $0.83 \pm 0.09$ ); methyl butyrate ( $3.30 \pm 0.25$ ); methyl valerate ( $4.83 \pm 0.55$ ); methyl caproate ( $7.15 \pm 0.70$ ). Our results are compared with the previous determinations and discussed in terms of structure–activity relationships.

## Introduction

Esters are a class of volatile organic compounds (VOCs) which is widely used as solvents in industry and in the manufacture of perfumes and flavorings. These compounds can be, then, emitted to the atmosphere. Esters, mainly formates and acetates, can also be produced in the atmosphere from the degradation of ethers [e.g. refs 1–3].

The atmospheric oxidation of these oxygenated VOCs which is initiated by the OH radical may significantly contribute to the formation of ozone and other components of the photochemical smog in urban areas. Kinetic and mechanistic information on OH-initiated oxidation is therefore needed, to assess the impact of these VOCs on air quality.

In this work, we report absolute rate constant data for the reaction of the OH radical with four aliphatic methyl esters: methyl propionate ( $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OCH}_3$ ), methyl butyrate ( $n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{OCH}_3$ ), methyl valerate ( $n\text{-C}_4\text{H}_9\text{C}(\text{O})\text{OCH}_3$ ), and methyl caproate ( $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OCH}_3$ ), in the temperature range 253–372 K:



The reported data are the first determination for the rate coefficients of reactions 3 and 4 at room temperature and for the temperature dependence of the rate coefficient for the four reactions. By extending the kinetic database for the OH + esters reactions, the purpose of this work was also to compare the rate coefficients of the methyl esters ( $\text{RC}(\text{O})\text{OCH}_3$ ) with those of acetates ( $\text{CH}_3\text{C}(\text{O})\text{OR}$ ), recently measured in our laboratory.<sup>4</sup>

## Experimental Section

The apparatus and the experimental methodology used have been described in detail previously,<sup>5,6</sup> and are briefly discussed

here. The pulsed laser photolysis – laser induced fluorescence (PLP–LIF) technique was used. OH radicals were produced by photolysis of  $\text{H}_2\text{O}_2$  at  $\lambda = 248 \text{ nm}$  (KrF excimer laser). The concentration of hydroxyl radicals was monitored at various reaction times ranging from ca. 10  $\mu\text{s}$  to 10 ms by pulsed laser induced fluorescence. A Nd:YAG pumped frequency doubled dye laser was used to excite the OH radical at  $\lambda = 282 \text{ nm}$ . Fluorescence from the OH radical was detected by a photomultiplier, fitted with a 309 nm narrow band-pass filter. The output pulse from the photomultiplier was integrated for a preset period by a gated charge integrator. Typically, the fluorescence signal from 100 probe laser shots were averaged to obtain one data (concentration, time) point and 10–15 delays were sampled to map out an OH profile over at least three lifetimes. The OH precursor ( $\text{H}_2\text{O}_2$ ), the ester, and the inert gas (helium) were flowed slowly through the cell, so that each photolysis/probe sequence encounters a fresh gas mixture and reaction products did not build up in the cell.

All experiments were carried out under pseudo-first-order conditions with  $[\text{ester}] \gg [\text{OH}]_0$ , the initial concentration of OH being  $[\text{OH}]_0 < 2 \times 10^{11} \text{ molecule cm}^{-3}$ . The temporal profiles of  $[\text{OH}]$ , therefore, followed the pseudo-first-order rate law:

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

$\text{X}_i$  refers to the ester in reaction  $i$  ( $i = 1\text{--}4$ ) and  $k_i$  is the rate coefficient for the reaction of OH with ester  $i$ . The decay rate,  $k'_0$ , is the first-order OH decay rate in the absence of the ester. The value of  $k'_0$  is essentially the sum of the reaction rate of OH with  $\text{H}_2\text{O}_2$ , and the diffusion rate of OH out of the detection zone. The concentration of OH at various reaction times (delay between the photolysis pulses and the probe pulses) was determined by measuring the LIF signals at those delay times. Weighted least-squares analysis (according to the signal-to-noise of the measured signal at the given time) was used to fit the data to the above equation and extract the values of  $k'$ . The second-order rate coefficients ( $k_i$ ) were obtained from the measured values of  $k'$  at various concentrations of esters.

The helium carrier gas (UHP certified to >99.9995% (Airphagas)) was used without purification. The 50 wt %  $\text{H}_2\text{O}_2$  solution obtained from Prolabo, was concentrated by bubbling helium through the solution to remove water for several days

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**TABLE 1: Reactions OH + Methyl Propionate (1), OH + Methyl Butyrate (2), OH + Methyl Valerate (3), OH + Methyl Caproate (4): Summary of Experimental Conditions and Measured  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$** 

$T$ (K)	[methyl propionate] ( $10^{14}$ ) <sup>a</sup>	$10^{13} \times (k_1 \pm 2\sigma)^b$	[methyl butyrate] ( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_2 \pm 2\sigma)^b$	[methyl valerate] ( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_3 \pm 2\sigma)^b$	[methyl caproate] ( $10^{14}$ ) <sup>a</sup>	$10^{12} \times (k_4 \pm 2\sigma)^b$
253	3.57–34.70	$8.71 \pm 0.47$						
253	5.68–60.20	$8.33 \pm 0.31^d$						
263	3.06–31.69	$8.46 \pm 0.24$	1.66–17.64	$4.08 \pm 0.16$	0.73–7.53	$6.96 \pm 0.23$		
263			1.62–15.38	$4.33 \pm 0.06$	1.49–14.16	$7.04 \pm 0.54^d$		
273	3.50–31.90	$8.68 \pm 0.32$	1.63–17.28	$3.97 \pm 0.09$	0.71–6.70	$6.36 \pm 0.16$	0.25–2.57	$8.40 \pm 0.30$
273			1.42–14.65	$4.03 \pm 0.06$			0.23–2.30	$8.67 \pm 0.37$
283			1.37–14.46	$3.69 \pm 0.06$	0.68–7.09	$5.57 \pm 0.30$	0.32–2.18	$8.02 \pm 0.22$
283					0.72–8.41	$6.03 \pm 0.20$		
295			1.30–13.66	$3.37 \pm 0.07$				
298	3.87–29.47	$8.52 \pm 0.45$	1.24–13.67	$3.37 \pm 0.04$	0.76–8.07	$4.76 \pm 0.09$	0.20–2.10	$7.03 \pm 0.34$
298	2.84–27.75	$8.00 \pm 0.29$	1.30–14.11	$3.32 \pm 0.08^c$	0.79–7.38	$4.89 \pm 0.15$	0.23–2.34	$7.25 \pm 0.13$
298	2.71–28.47	$8.41 \pm 0.29^f$	2.65–25.25	$3.21 \pm 0.06^d$	0.55–6.28	$5.05 \pm 0.15$	0.43–4.10	$7.72 \pm 0.20^d$
298					1.43–13.71	$4.63 \pm 0.31^e$	0.48–4.69	$6.53 \pm 0.18^e$
323	2.59–26.01	$8.43 \pm 0.50$	1.39–14.66	$2.84 \pm 0.10$	0.53–5.67	$4.78 \pm 0.15$	0.19–1.98	$7.00 \pm 0.32$
348	2.93–25.42	$9.50 \pm 0.42$	1.26–13.69	$2.83 \pm 0.14$	0.70–6.98	$4.35 \pm 0.11$	0.18–1.82	$6.11 \pm 0.24$
372	2.82–23.51	$10.6 \pm 0.4$	1.27–12.87	$2.89 \pm 0.05$	0.68–6.42	$4.31 \pm 0.13$	0.17–1.82	$5.91 \pm 0.22$
372	4.62–46.50	$10.1 \pm 0.3^e$	2.19–21.78	$2.84 \pm 0.11^e$	0.47–4.95	$4.50 \pm 0.25^f$	0.16–1.69	$6.38 \pm 0.18^f$

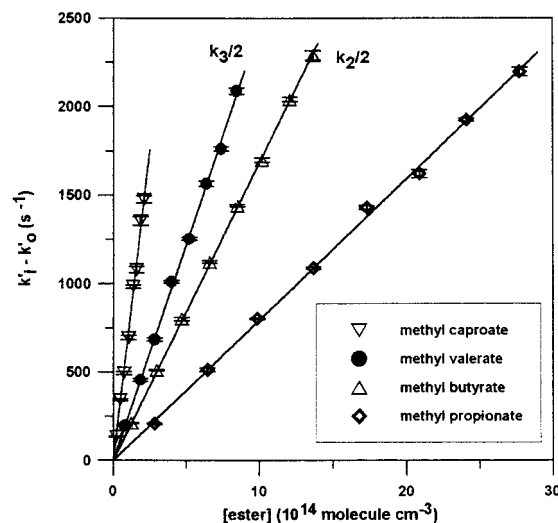
<sup>a</sup> Units of molecule  $\text{cm}^{-3}$ . <sup>b</sup> Units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>c</sup> Variation of the photolysis laser fluence (decrease by a factor of 3). <sup>d</sup> Variation of flow velocity (decrease by a factor of 3). <sup>e</sup> Experiments carried out at 300 Torr. <sup>f</sup> Variation of the photolysis laser fluence (decrease by a factor of 2).

prior to use to remove water, 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 containing  $\text{H}_2\text{O}_2$ . Methyl propionate (99%), methyl butyrate (99%), methyl valerate (99%) and methyl caproate (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 ester was premixed with helium in a 10 L glass light-tight bulb to form (0.3–4.8)% mixture at a total pressure of about 800 Torr. All the gases were flowed into the reactor through Teflon tubing. The gas mixture containing the ester,  $\text{H}_2\text{O}_2$ , and the bath gas (approximately 100 Torr of helium) were flowed through the cell with a linear velocity ranging between 1 and 3  $\text{cm s}^{-1}$ . The concentration of the ester was calculated from its mass flow rate, temperature, and 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

The concentration ranges of the esters were as follows: methyl propionate:  $(2.59\text{--}60.20) \times 10^{14}$ , methyl butyrate:  $(1.24\text{--}25.25) \times 10^{14}$ , methyl valerate:  $(0.47\text{--}14.16) \times 10^{14}$ , methyl caproate:  $(0.16\text{--}4.69) \times 10^{14}$  (units of molecule  $\text{cm}^{-3}$ ). The initial concentration of OH radicals was lower than  $2 \times 10^{11}$  molecule  $\text{cm}^{-3}$ . Possible contribution to the measured rate constants from secondary reactions of OH with the products of reactions (1–4) was then significantly reduced by using high ratios ( $10^2\text{--}10^4$ ), of [ester]/[OH] which did not show any difference in measured  $k_i$  values. The rate constants were also shown to be independent of variations in the flow velocity ( $v = 1\text{--}3 \text{ cm/s}$ ) through the cell, changes in the total pressure of the system ( $P = 100\text{--}300 \text{ Torr}$ ), or variations in the photolysis laser fluence ( $E = 2\text{--}6 \text{ mJ}$ ). Values of  $k_i$  were derived from the least-squares fit of the straight lines. Figure 1 shows the plots of  $(k'_i - k'_0)$  versus the ester concentration obtained at room temperature for the different esters. The quoted errors for  $k_i$  determined in this work include  $2\sigma$  from the least-squares analysis and the estimated systematic error 5% (due to uncertainties in measured concentrations).



**Figure 1.** Plots of  $(k'_i - k'_0)$  to  $(k'_4 - k'_0)$  vs methyl ester concentration at room temperature. The lines represent the linear least-squares fitting.

The experimental conditions and the measured values of the rate coefficients  $k_1\text{--}k_4$  over the temperature range 253–372 K are listed in Table 1. They are also shown in Figure 2 in the conventional form of the Arrhenius equation ( $k = Ae^{-E_a/RT}$ ). The plots show a slight negative temperature dependence of the rate constant for all the methyl esters, except for methyl propionate, for which a slight positive temperature dependence was observed. Moreover, all the plots appear to exhibit slight curvature. The Arrhenius parameters for the OH reactions with the esters are given in Table 2 together with the results reported at room temperature in previous studies.

For all these compounds, the present work provides the first temperature dependence of the rate coefficients for their reaction with the OH radical. The rate coefficient at 298K,  $k_3$  and  $k_4$ , for methyl valerate and methyl caproate are also the first to be reported. For methyl propionate and methyl butyrate, our data at room temperature are in good agreement with those obtained by Wallington et al.<sup>7</sup> using the absolute flash photolysis–resonance fluorescence technique. In contrast, for methyl propionate our  $k_1$  determination disagrees with that of Campbell and Parkinson,<sup>8</sup> which is three times lower. This latter was obtained using a relative rate method.

TABLE 2: Comparison of OH Reaction Rate Coefficients with Previous Work

molecule	T, K	$k,^a 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$A,^b 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$E/R,^b \text{ K}$	T range, K	technique <sup>c</sup>	ref
C <sub>2</sub> H <sub>5</sub> C(O)OCH <sub>3</sub>	292	0.27 ± 0.11				RR	8
	296	1.03 ± 0.04				FP-RF	7
	298	0.83 ± 0.09	(1.45 ± 0.42)	(148 ± 86)	253–372	LP-LIF	this work
C <sub>3</sub> H <sub>7</sub> C(O)OCH <sub>3</sub>	296	3.04 ± 0.33				FP-RF	7
	298	3.30 ± 0.25	(0.96 ± 0.29)	-(380 ± 91)	263–372	LP-LIF	this work
C <sub>4</sub> H <sub>9</sub> C(O)OCH <sub>3</sub>	298	4.83 ± 0.55	(1.37 ± 0.64)	-(401 ± 142)	263–372	LP-LIF	this work
C <sub>5</sub> H <sub>11</sub> C(O)OCH <sub>3</sub>	298	7.15 ± 0.70	(2.46 ± 1.04)	-(326 ± 130)	273–372	LP-LIF	this work

<sup>a</sup> Errors are those given by the authors. <sup>b</sup> For our data, the uncertainties for  $A$  and  $E/R$  were given by  $\Delta A = 2A\sigma_{\ln A}$  and  $\Delta E/R = 2\sigma_{E/R}$  for the Arrhenius forms. <sup>c</sup> Key: LP-LIF, laser photolysis-laser induced fluorescence; FP-RF, flash photolysis-resonance fluorescence; RR, relative rate.

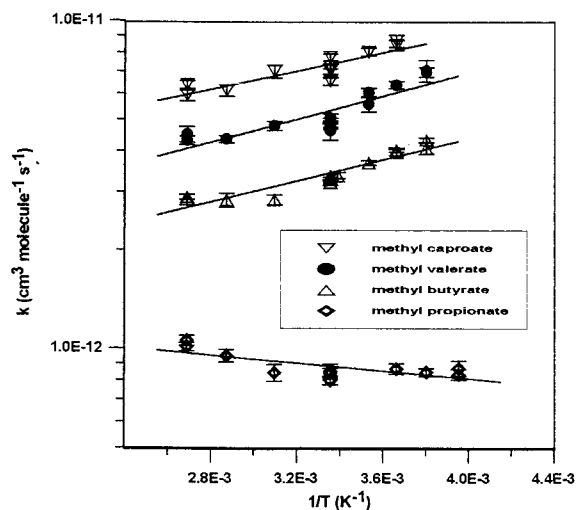


Figure 2. Plots of  $k_1$  to  $k_4$  vs  $1/T$ . The solid lines represent the Arrhenius parameter least-squares fits to the individual data points for each ester. The error bars of the individual points are  $2\sigma$  and do not include estimated systematic errors.

**Trends in the OH + Esters Reaction Rate Constants.** The present rate constant values  $k_1$ – $k_4$  can be compared with those calculated from the updated structure–activity relationship (SAR) of Atkinson based on group reactivity.<sup>9</sup> In a first calculation the substituent factor  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR})$  was considered to be equal to  $F(-\text{CH}_2-)$ , i.e.,  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = F(-\text{CH}_2-) = 1.23$ . In this case, it is assumed that the  $-\text{C}(\text{O})\text{OR}$  group has no influence on the  $\text{CH}_2$  or  $\text{CH}_3$  group in  $\beta$  position in the acyl end of the ester. The calculated  $k_1$ – $k_4$  values, compared to the experimental ones, are in brackets:  $k_1 = 0.83$  (1.08);  $k_2 = 3.30$  (2.38);  $k_3 = 4.83$  (3.80);  $k_4 = 7.15$  (5.21) (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K). The calculated rate constants are ca. 20 to 30% lower than the experimental ones except for  $k_1$  (methyl propionate) where the calculated value exceeds the experimental value one by ca. 20%. In a second calculation it was assumed that the  $-\text{C}(\text{O})\text{OR}$  group had the same influence on the  $\text{CH}_2$  or  $\text{CH}_3$  group in  $\beta$  position in the acetyl end of the ester as the ketone group  $-\text{C}(\text{O})\text{R}$ ; i.e.,  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = F(-\text{CH}_2-\text{C}(\text{O})\text{R}) = 3.9$ . The compared experimental and calculated (in brackets)  $k_1$ – $k_4$  values are now as follows:  $k_1 = 0.83$  (1.44);  $k_2 = 3.30$  (4.88);  $k_3 = 4.83$  (6.86);  $k_4 = 7.15$  (8.28) (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K). In this case all the calculated values are (ca. 15 to 80%) higher than experimental ones.

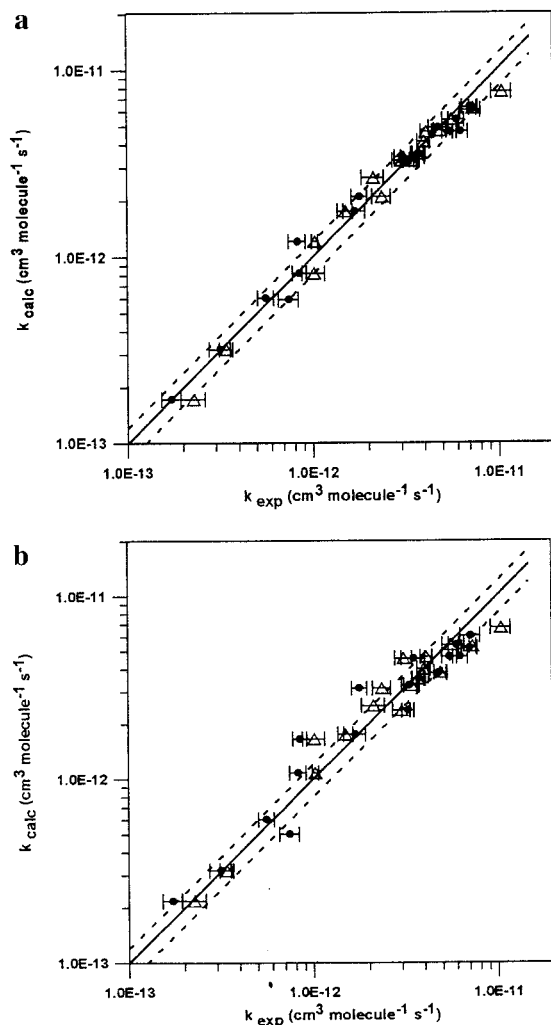
Regarding the significant differences between experimental and calculated values, these calculations suggest that a specific substituent factor  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR})$  can be defined to calculate the reactivities of the  $\text{CH}_2$  or  $\text{CH}_3$  group in  $\beta$  position of  $-\text{C}(\text{O})\text{OR}$  in esters. The calculations also indicate that the  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR})$  value is between 1.23 ( $F(-\text{CH}_2-)$ ) and 3.9 ( $F(-\text{CH}_2-\text{C}(\text{O})\text{R})$ ).

By fitting the calculated and experimental rate constant values, the following  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR})$  values are derived from  $k_2$ ,  $k_3$  and  $k_4$ , respectively: 2.21, 2.17, and 2.96. Considering that the sensitivity of  $k_4$  to  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR})$  is lower than that of  $k_2$  and  $k_3$ , the value proposed is taken as  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 2.2$ . Using this latter, the compared experimental and calculated (in brackets)  $k_1$ – $k_4$  values become:  $k_1 = 0.83$  (1.21);  $k_2 = 3.30$  (3.29);  $k_3 = 4.83$  (4.91);  $k_4 = 7.15$  (6.32) (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K).

The present value  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 2.2$  and the recent determinations:  $F(-\text{O}-\text{C}(\text{O})\text{H}) = 0.6$  and  $k(\text{H}-\text{C}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from this laboratory,<sup>10</sup> together with existing data  $F(-\text{C}(\text{O})\text{OR}) = 0.74$  and  $F(-\text{OC}(\text{O})\text{R}) = 1.6$ , have been used to calculate rate constants at 298 K for a series of 23 esters, for which experimental rate constants are available for comparison. The experimental rate constants are from the present work and previous studies from this laboratory,<sup>4,10,11</sup> and from the extensive work of ref 7. These experimental and calculated rate constants are reported in Table 3. The calculated values using the substituent factors from Kwok and Atkinson<sup>9</sup> are also reported:  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 1.23$ ,  $F(-\text{O}-\text{C}(\text{O})\text{H}) = 1.6$  and  $k(\text{H}-\text{C}(\text{O})\text{OR})$  considered as negligible. The plots of the present calculated values against experimental ones,  $\log k_{\text{calc}}$  vs  $\log k_{\text{exp}}$  are shown in Figure 3a. Figure 3b gives similar plots where  $k_{\text{calc}}$  are calculated using the substituent factors from Kwok and Atkinson.<sup>9</sup> The comparison of both figures show a slightly better correlation in Figure 3a.

Besides, it is interesting to compare the rate constants at 298 K for methyl esters,  $\text{R}-\text{C}(\text{O})\text{OCH}_3$  and acetates,  $\text{CH}_3\text{C}(\text{O})\text{OR}$ , containing the same R group. Experimental data are reported in Table 4 for methyl esters and acetates containing the same R: R = C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub> and *n*-C<sub>5</sub>H<sub>11</sub>. The table shows that for R = *n*-C<sub>3</sub>H<sub>7</sub>, *n*-C<sub>4</sub>H<sub>9</sub> and *n*-C<sub>5</sub>H<sub>11</sub>, the rate constants are comparable for methyl esters and acetates. The calculated values (Table 3 with modified SAR) are also comparable:  $k_{\text{calc}}(\text{R}-\text{C}(\text{O})\text{OCH}_3)$ ;  $k_{\text{calc}}(\text{CH}_3-\text{C}(\text{O})\text{OR})$  are respectively: 3.29; 3.26 (R = *n*-C<sub>3</sub>H<sub>7</sub>), 4.91; 4.67 (R = *n*-C<sub>4</sub>H<sub>9</sub>) and 6.32; 6.08 (R = *n*-C<sub>5</sub>H<sub>11</sub>) (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Similar rate constant is expected from such a calculation for methyl esters and acetates having similar alkyl group R with C > 5 since the resulting reactivity increment,  $\Delta k$ , is the same, i.e., it is obtained by adding one CH<sub>2</sub> to the R group of either the methyl ester or the acetate ( $\Delta k = k_{\text{CH}_2} \times (F(-\text{CH}_2-))^2 = 0.934 \times (1.23)^2 = 1.4$ ) (units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>9</sup>

In contrast with the above methyl esters and acetates, methyl propionate and ethyl acetate (R = C<sub>2</sub>H<sub>5</sub>) have a different reactivity toward OH. The two times lower rate constant of methyl propionate can be explained by the deactivating effect of the  $-\text{C}(\text{O})\text{OR}$  group on the  $\text{CH}_2$  group in  $\alpha$  position while the  $-\text{OC}(\text{O})\text{R}$  group activates the  $\text{CH}_2$  group in  $\alpha$  position in the ethyl acetate molecule. This is reflected by the different

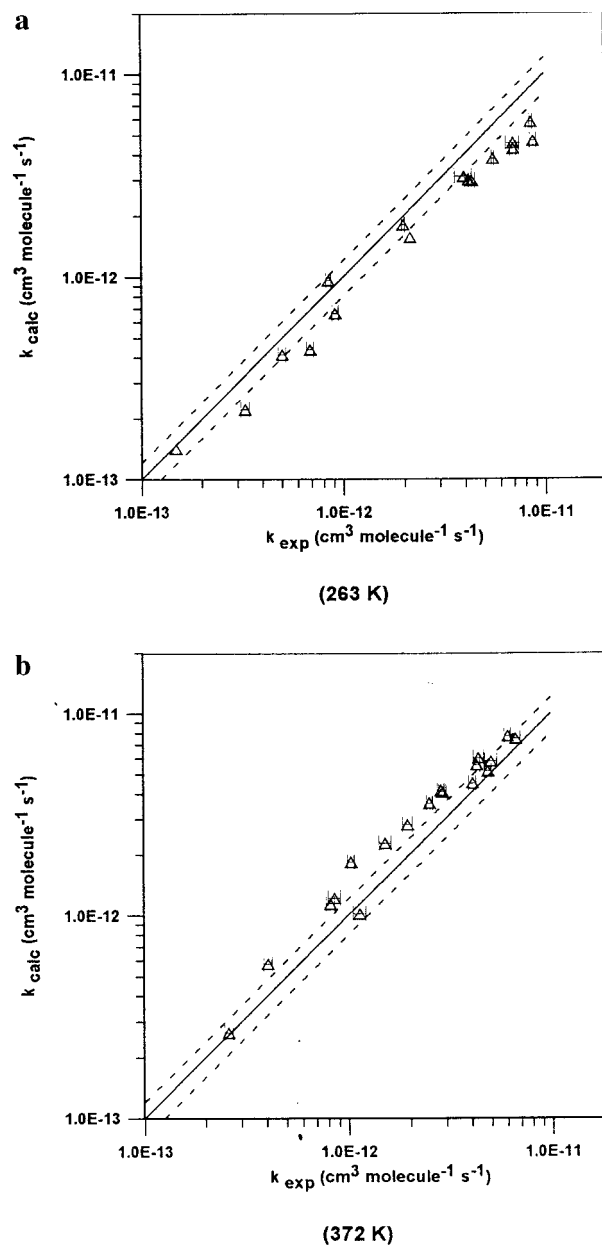


**Figure 3.** Comparison of the experimental,  $k_{\text{exp}}$ , and calculated,  $k_{\text{calc}}$ , rate constants at 298 K for OH reaction with 23 esters (see text). Experimental data are: (●) from this laboratory [this work, refs 4, 10, 11], (Δ) from ref 7. The dashed lines correspond to a departure of 20% from the best fit (solid line). (a) The substituent factors are:  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 2.2$  (this work),  $F(-\text{OC}(\text{O})\text{H}) = 0.6$  [ref 10],  $k(\text{H}-\text{C}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [ref 10],  $F(-\text{C}(\text{O})\text{OR}) = 0.74$  and  $F(-\text{OC}(\text{O})\text{R}) = 1.6$  [9]. (b)  $F(-\text{C}(\text{O})\text{OR}) = 0.74$ ;  $F(-\text{OC}(\text{O})\text{R}) = 1.6$ , and  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 1.23$  [ref 9].

values of the corresponding substituent factors:  $F(-\text{C}(\text{O})\text{OR}) = 0.74$  compared to  $F(-\text{OC}(\text{O})\text{R}) = 1.6$ .<sup>9</sup>

The rate constant database for aliphatic acetates and methyl esters might also be used in a simple way to estimate rate constants for other esters. The rate constant for an ester  $\text{R}_1\text{C}(\text{O})\text{OR}_2$  is assumed to be the sum,  $k(\text{R}_1) + k(\text{R}_2)$ ,  $k(\text{R}_1)$  and  $k(\text{R}_2)$  being the partial rate constants for the acyl end and alkoxy end of the ester, respectively.  $k(\text{R}_1)$  and  $k(\text{R}_2)$  are derived from the experimental rate constant data for methyl esters and acetates:  $k(\text{R}_1) = k_{\text{exp}}(\text{R}_1\text{C}(\text{O})\text{OCH}_3) - k(\text{CH}_3)$ , ( $k(\text{CH}_3) = 2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ),<sup>9</sup> and  $k(\text{R}_2) = k_{\text{exp}}(\text{CH}_3\text{C}(\text{O})\text{OR}_2) - k'(\text{CH}_3)$ , ( $k'(\text{CH}_3) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>11</sup> The calculated rate constants for OH reactions with esters  $\text{R}_1\text{C}(\text{O})\text{OR}_2$  agree well with the experimental ones for small  $\text{R}_1$  and  $\text{R}_2$  alkyl groups but some differences appear for larger ones (e.g. 20% for *n*-butyl butyrate). The application of this method may however be limited since it assumes that  $\text{R}_1$  and  $\text{R}_2$  groups do not interact, which is not certain.

**Temperature Dependence of the OH + Acetate Reaction Rate Constants.** The negative temperature dependence observed in the temperature range of the study for  $k_2$ – $k_4$  is similar



**Figure 4.** Comparison of the experimental,  $k_{\text{exp}}$ , and calculated,  $k_{\text{calc}}$ , rate constants for OH reaction with 23 esters (see text) at  $T = 263 \text{ K}$  (Figure 4a) and  $372 \text{ K}$  (Figure 4b). Experimental data are from this laboratory [refs 4, 10, 11, and this work]. The dashed lines correspond to a departure of 20% from the best fit (solid line). For SAR calculated data, parameters used are from ref 9 except the following substituent factors derived from our work:  $F(-\text{CH}_2-\text{C}(\text{O})\text{OR}) = 2.2$  (this work),  $F(-\text{OC}(\text{O})\text{H}) = 0.6$  [ref 10],  $k(\text{H}-\text{C}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [ref 10].

to that observed for the rate constants of OH reaction with ethers, formates and acetates containing  $\text{CH}_2$  or  $\text{CH}$  groups.<sup>6,10–12</sup> In contrast, a slight positive temperature dependence of the rate constants have been observed in previous studies for OH reaction with ethers and esters containing only  $\text{CH}_3$  groups. This is the case for dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ), methyl *tert*-butyl ether ( $\text{CH}_3\text{OC}(\text{CH}_3)_3$ ), methyl formate ( $\text{HC}(\text{O})\text{OCH}_3$ ), *tert*-butyl formate ( $\text{HC}(\text{O})\text{OC}(\text{CH}_3)_3$ ), methyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ ), *tert*-butyl acetate ( $\text{CH}_3\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$ ).<sup>4,6,10–12</sup> A slight positive temperature dependence is also observed in the present study for the rate constant  $k_1$  of the reaction of OH with  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OCH}_3$ . This indicates that the  $\text{CH}_2$  group in the  $\alpha$  position of a carbonyl group, which is strongly deactivated, does not influence the temperature dependence of the rate constant as it is the case for the ethers, formates and acetates

TABLE 3: Comparison of Rate Coefficients for Different Esters between Experimental and Calculated Values

compound	$10^{12} \times k_{\text{exp}}^{a,b}$	$10^{12} \times k_{\text{exp}}^{a,c}$	$10^{12} \times k_{\text{calc}}^{a,d}$ SAR	$10^{12} \times k_{\text{calc}}^{a,e}$ modified SAR
methyl formate	0.173 ± 0.021	0.227 ± 0.034	0.218	0.172
ethyl formate	0.852 ± 0.075	1.02 ± 0.14	1.66	0.818
<i>n</i> -propyl formate	1.80 ± 0.17	2.38 ± 0.27	3.15	2.10
<i>n</i> -butyl formate	3.54 ± 0.52	3.12 ± 0.33	4.57	3.42
<i>tert</i> -butyl formate	0.746 ± 0.091		0.502	0.593
methyl acetate	0.322 ± 0.026	0.341 ± 0.029	0.319	no change
ethyl acetate	1.67 ± 0.22	1.51 ± 0.14	1.76	no change
<i>n</i> -propyl acetate	3.42 ± 0.26	3.45 ± 0.34	3.26	no change
<i>n</i> -butyl acetate	5.52 ± 0.51	4.15 ± 0.30	4.67	no change
<i>n</i> -pentyl acetate	7.34 ± 0.91		6.08	no change
isopropyl acetate	3.77 ± 0.29	3.72 ± 0.29	3.55	no change
isobutyl acetate	6.33 ± 0.52		4.67	no change
<i>sec</i> -butyl acetate	6.04 ± 0.58	5.65 ± 0.59	5.41	no change
<i>tert</i> -butyl acetate	0.56 ± 0.05		0.604	no change
methyl propionate	0.831 ± 0.087	1.03 ± 0.04	1.08	1.21
ethyl propionate		2.14 ± 0.30	2.52	2.65
<i>n</i> -propyl propionate		4.02 ± 0.32	4.01	4.14
methyl butyrate	3.30 ± 0.25	3.04 ± 0.33	2.38	3.29
ethyl butyrate		4.94 ± 0.38	3.83	4.73
<i>n</i> -propyl butyrate		7.41 ± 0.32	5.32	6.23
<i>n</i> -butyl butyrate		10.6 ± 1.3	6.73	7.64
methyl valerate	4.83 ± 0.55		3.80	4.91
methyl caproate	7.15 ± 0.70		5.21	6.32

<sup>a</sup> Units of molecule cm<sup>-3</sup>. <sup>b</sup> Our values [refs 4, 10, 11, and this work]. <sup>c</sup> Values from ref 7. <sup>d</sup> SAR [ref 9]. <sup>e</sup> Modified SAR:  $F(-\text{CH}_2\text{C}(\text{O})\text{OR}) = 2.2$ ;  $F(-\text{OC}(\text{O})\text{H}) = 0.6$ ;  $k(\text{HC}(\text{O})\text{OR}) = 0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [ref 10, and this work].

TABLE 4: Comparison of Rate Coefficients for Methyl Esters and Acetates Containing the Same Alkyl Group R

R	$10^{12} \times k_{\text{R}-\text{C}(\text{O})\text{OCH}_3^a}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$10^{12} \times k_{\text{CH}_3-\text{C}(\text{O})\text{OR}^b}$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
C <sub>2</sub> H <sub>5</sub>	0.83	1.67
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	3.30	3.42
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	4.83	5.52
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	7.15	7.34

<sup>a</sup> Data obtained in this work. <sup>b</sup> Data from ref 4.

already investigated<sup>4,6,10-12</sup> where the CH<sub>2</sub> group is located on the alkoxy end of the molecule. For methyl butyrate, methyl valerate, and methyl caproate the negative temperature dependence of  $k_2$ ,  $k_3$  and  $k_4$ , respectively, is due to the presence of at least one CH<sub>2</sub> group in  $\beta$  position, which does not seem to be deactivated by the carbonyl group as CH<sub>2</sub> in methyl propionate. The present data for the temperature dependence of  $k_1$  are also consistent with the slightly positive temperature dependence recently observed for the rate constant of the reaction of OH with 2-butanone (CH<sub>3</sub>CH<sub>2</sub>C(O)CH<sub>3</sub>) which also contains only one CH<sub>2</sub>, in  $\alpha$  position of a carbonyl group.<sup>13</sup>

The experimental Arrhenius expressions of the rate constants obtained in our laboratory for OH reaction with esters [refs 4, 10, 11, and this work] have been compared with the calculated expressions from SAR.<sup>9</sup> It is observed that the experimental,  $E/R$ , temperature factors are lower than the calculated ones, except for methyl formate. The calculated  $E/R$  factors from SAR are all positive while the experimental ones are negative for compounds containing not only CH<sub>3</sub> groups. In the temperature range investigated, this may indicate the occurrence of an alternative channel in parallel to the direct H-atom transfer considered in SAR. This additional channel may involve the formation of a long-lived adduct intermediate as already suggested.<sup>4,6,10-12</sup> The experimental versus SAR calculated rate constants are plotted at  $T = 263 \text{ K}$  (Figure 4a) and  $T = 372 \text{ K}$  (Figure 4b) representing the limits of the temperature range investigated. The plots show that most of the calculated values are lower than the experimental ones by more than 20% at the

lowest temperature. In contrast, most of the calculated values are higher by 20% at the highest temperature.

**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 esters which react predominantly with the OH radical. With a typical tropospheric OH concentration of  $1 \times 10^6$  molecule cm<sup>-3</sup> the following tropospheric lifetimes ( $\tau = 1/k_1[\text{OH}]$ ) are estimated: 14 days, 3.5 days, 2.4 days, and 1.6 day for methyl propionate, methyl butyrate, methyl valerate, and methyl caproate, respectively.

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