Absolute Rate Constants for the Reactions of Cl Atoms with a Series of Esters

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Absolute rate coefficient measurements have been carried out for the Cl atom reaction with a series of esters, at room temperature (298 ± 2 K) and in the pressure range 15−60 Torr, using the laser photolysis−resonance fluorescence technique. The rate coefficients obtained (in units of cm^3 $molecule^{-1}$ s^{-1}) are as follows: methyl formate $(1.83 \pm 0.21) \times 10^{-12}$, ethyl formate $(1.34 \pm 0.15) \times 10^{-11}$, *n*-propyl formate $(5.63 \pm 0.65) \times 10^{-11}$, *n*-butyl formate $(1.41 \pm 0.17) \times 10^{-10}$, methyl acetate $(2.85 \pm 0.35) \times 10^{-12}$, ethyl acetate $(2.01 \pm 0.25) \times 10^{-11}$, *n*-propyl acetate $(7.76 \pm 0.92) \times 10^{-11}$, *n*-butyl acetate $(1.74 \pm 0.20) \times 10^{-10}$, isopropyl acetate $(2.68 \pm 0.34) \times 10^{-11}$, isobutyl acetate $(1.08 \pm 0.13) \times 10^{-10}$, *tert*-butyl acetate $(2.42 \pm 0.28) \times 10^{-11}$, *sec*-butyl acetate $(9.1 \pm 1.0) \times 10^{-11}$, methyl propionate $(1.98 \pm 0.26) \times 10^{-11}$, methyl butyrate $(8.6 \pm 0.9) \times 10^{-11}$, methyl valerate $(1.7 \pm 0.2) \times 10^{-10}$, and methyl caproate $(2.72 \pm 0.32) \times 10^{-10}$. The results are discussed in terms of structure−reactivity relationship.

Introduction

The atmospheric degradation of most organic compounds is initiated by reaction with OH radicals.[1] However, chlorine atom reaction with organic compounds is now considered of potential importance in the marine troposphere where significant chlorine atom concentrations may be present [e.g., refs 2−6]. The major source of chlorine atoms would be heterogeneous processes of NaCl contained in sea salt particles [e.g., refs 7 and 8]. Besides, the reaction of volatile organic compounds (VOCs), especially oxygenated ones, with Cl atoms is currently used instead of the OH reaction to initiate the atmospheric oxidation of those compounds in smog chambers experiments. In general, Cl and OH have similar modes of attack in their reactions with organic compounds, and Cl generally reacts much more rapidly than OH does, making in some cases reaction time more compatible with the time constants of the smog chamber experiments.

To assess the importance of the chemical degradation of VOCs through reaction with Cl atoms and to investigate the atmospheric Cl atom initiated oxidation of VOCs in smog chamber experiments to mimic OH-initiated oxidation, reliable reaction rate coefficient data are needed for the reactions of Cl atoms with VOCs. Several studies have been carried out recently on Cl atom reaction with hydrocarbons (alkanes, alkenes, dialkenes) [e.g., refs 9−14]. Studies of Cl reaction with oxygenated VOCs have dealt with alcohols, ethers, aldehydes and ketones [e.g., ref 15 and references therein]. For Cl atom reaction with esters, which is the subject of the present work, no data have been reported so far except relative rate data for the Cl + methyl formate reaction.[16] Esters represent an important class of oxygenated VOCs, which are used as food flavorings and in perfumes. They are also present in some fruits and can be then emitted to the atmosphere naturally. They are also formed as intermediate species during the tropospheric degradation reactions of volatile organic compounds such as ethers [e.g., refs 17−21].

We report herein room-temperature rate coefficients for the reactions of Cl with the following esters: methyl formate, ethyl formate, *n*-propyl formate, *n*-butyl formate, methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, isopropyl acetate, isobutyl acetate, *sec*-butyl acetate, *tert*-butyl acetate, methyl propionate, methyl butyrate, methyl valerate, and methyl caproate. The present work also aims at extending the kinetic database to be used to develop structure−reactivity relationships for Cl reaction with VOCs, especially for oxygenated ones.

Experimental Section

The experimental technique of pulsed laser photolysis−resonance fluorescence (PLP−RF) was used in this study. Details of the technique and a description of the apparatus have been given previously.[22] Therefore, only the information necessary to understand this work is presented here.

The reaction cell is constructed of Pyrex and has an internal volume of about 200 cm^3. The radiation ($\lambda \sim 135$ nm) from a microwave-driven lamp, through which He containing a low concentration of Cl_2 (0.2−0.3%) was flowed, was used to excite the resonance fluorescence from Cl in the cell. The lamp was situated perpendicular to the photolysis laser beam. A CaF_2 window was placed between the lamp and the cell. Chlorine atoms were produced by photolyzing Cl_2 at 355 nm using a pulsed, frequency-tripled, Nd:YAG laser. The resonance fluorescence radiation was collected at 90° to both the resonance lamp and photolysis laser beam by two CaF_2 lenses and imaged onto the photocathode of a solar blind photomultiplier tube. The regions between the two lenses and between the last lens and the photomultiplier were evacuated.

Signals were obtained using photon-counting techniques in conjunction with multichannel scaling. The fluorescence signal from the PMT was processed by a digitizer and sent to an EG&G multichannel scaler to collect the time-resolved signal. The multichannel scaler was coupled to a microcomputer for imaging and analysis of the signals. Data acquisition was started prior to the photolysis pulse to obtain the background level of scattered light. A delay generator pretriggered the acquisition before triggering the laser pulse. The background was sub-

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tracted from the postphotolysis signal to obtain the temporal profiles of the Cl atom concentrations. The Cl temporal profiles following 5000−40000 laser pulses were coadded to enhance the signal-to-noise ratio. The detection limit for Cl atoms defined as $S/\sqrt{B} = 1$, (where S is the signal and B the background) was around 8×10^9 atoms cm^{-3} for 1 s integration time.

To avoid accumulation of photolysis or reaction products, the experiments were carried out under slow flow conditions. The linear flow velocity through the cell was in the range 2−4 cm s^{-1}, and the repetition rate of the photolysis laser was 10 Hz. Esters and Cl_2 were flowed from 10 L bulbs containing dilute mixtures in helium. Concentrations of the different gases in the cell were calculated from measurements of the appropriate mass flow rates and total pressure. For each ester, two different mixtures (ester/He) were used to determine the rate coefficient.

The chemicals had the following purities: He (UHP certified to >99.9995%, Alphagaz), the carrier gas, was passed from tank to cell through a liquid nitrogen trap. Cl_2 (99.8%, UCAR) was degassed several times at 77 K before use. O_2 was certified to >99.995% (Alphagaz). Methyl formate (>99%) ethyl formate (>98%), *n*-butyl acetate (>99%), isopropyl acetate (≥99.5%), and isobutyl acetate (99%) were from Fluka; *n*-propyl formate (≈98.7%), *n*-butyl formate (>97%), methyl acetate (99%), ethyl acetate (99.8%), *n*-propyl acetate (99%), *sec*-butyl acetate (≥99%), *tert*-butyl acetate (≥99%), methyl prioponate (99%), methyl butyrate (99%), methyl valerate (99%), and methyl caproate (99%) were from Aldrich. These compounds were further purified by repeated freeze−pump−thaw cycles and fractional distillation before use between the liquid nitrogen temperature and −10 °C. The different mixtures (ester/He) were systematically analyzed with a GC/FID/MS.

Results and Discussion

The rate coefficients for the studied reactions have been measured at (298 ± 2) K:

$$Cl + RC(O)OR' \rightarrow \text{products} \qquad k$$

The rate coefficients were numbered as follows: $k_1(HC(O)OCH_3)$, $k_2(HC(O)OCH_2CH_3)$, $k_3(HC(O)O(CH_2)_2CH_3)$, $k_4(HC(O)O(CH_2)_3CH_3)$, $k_5(CH_3C(O)OCH_3)$, $k_6(CH_3C(O)OCH_2CH_3)$, $k_7(CH_3C(O)O(CH_2)_2CH_3)$, $k_8(CH_3C(O)O(CH_2)_3CH_3)$, $k_9(CH_3C(O)OCH(CH_3)_2)$, $k_{10}(CH_3C(O)OCH_2CH(CH_3)_2)$, $k_{11}(CH_3C(O)OC(CH_3)_3)$, $k_{12}(CH_3C(O)OCH(CH_3)C_2H_5)$, $k_{13}(CH_3CH_2C(O)OCH_3)$, $k_{14}(CH_3(CH_2)_2C(O)OCH_3)$, $k_{15}(CH_3(CH_2)_3C(O)OCH_3)$, and $k_{16}(CH_3(CH_2)_4C(O)OCH_3)$.

The reactions were studied under pseudo-first-order conditions using a large excess of the esters over Cl atoms. Typically, the initial Cl atom concentration, $[Cl]_0$, was around 5×10^{11} atoms cm^{-3}. With a reaction mixture containing Cl_2, ester (RC(O)OR′), and helium, the temporal profile of Cl atoms is governed by the following processes:

$$Cl + \text{ester} \rightarrow \text{products} \qquad k$$

$$Cl \rightarrow \text{loss by diffusion} \qquad k_{dif}$$

Under these conditions and in the absence of secondary reactions, the Cl atom concentration profile should follow a simple exponential rate law:

$$[Cl]_t = [Cl]_0 \exp(-k't) \qquad \text{with} \quad k' = k[\text{ester}] + k_{dif}$$

where k' is the pseudo-first-order rate constant and [ester] is the ester concentration. k_{dif} is the first-order decay rate of Cl atoms in the absence of the ester. k_{dif} represents the diffusion rate of Cl atoms out of the detection zone and reaction with background impurities. k is the rate coefficient for the reaction of Cl atoms with the ester. Yet, preliminary experiments showed that the Cl decays in the presence of the esters were biexponential. This behavior was attributed to regeneration of Cl via the secondary reaction:

$$R'' + Cl_2 \rightarrow R''Cl + Cl$$

where R″ is the radical formed in the initial reaction Cl + RC(O)OR′. To make this secondary reaction negligible, an oxygen concentration up to 1×10^{16} molecules cm^{-3} was added to the reaction mixture. The chlorine atom decays were then monoexponential, showing that the radical R″ reacts predominantly with O_2 and not with Cl_2 under these experimental conditions ($[Cl_2] = (3-5) \times 10^{13}$ molecules cm^{-3}). This observation is consistent with the rate ratio $k_{(R''+O_2)}[O_2]/k_{(R''+Cl_2)}[Cl_2]$ higher than 20, which can be estimated with $[O_2]/[Cl_2] = 2 \times 10^2$, and taking $k_{(R''+O_2)}/k_{(R''+Cl_2)} \geq 0.1$. The estimation for the latter ratio ($k_{(R''+O_2)}/k_{(R''+Cl_2)} \geq 0.1$) is based on existing data for $k_{(CH_3CO\ +\ O_2)}/k_{(CH_3CO\ +\ Cl_2)} = 0.13$[23] and $k_{(CH_3OC(O)OCH_2\ +\ O_2)}/k_{(CH_3OC(O)OCH_2\ +\ Cl_2)} = 0.5$.[24]

On the other hand, the addition of O_2 decreased the detection sensitivity of Cl atoms, O_2 being an efficient quencher and absorber of the fluorescence of Cl atoms. Thus, the concentration of added O_2 was limited to $\sim 1 \times 10^{16}$ molecules cm^{-3}. Few experiments were performed with $[O_2] \sim 2 \times 10^{16}$ molecules cm^{-3} for a limited range of ester concentrations, and the obtained rate coefficients for Cl + ester reactions were similar to those obtained with $[O_2] \sim 1 \times 10^{16}$ molecules cm^{-3}. Then, this latter concentration was considered to be suitable to prevent the R″ + Cl_2 reaction without decreasing too much the detection sensitivity of Cl atoms.

The experimental conditions and the measured values of the rate coefficients k_1-k_{16} are listed in Table 1. All experiments were performed at a total pressure of 15 and 60 Torr. The diffusion rate of Cl out of the detection zone (k_{dif}) was around 35 s^{-1} for the experiments carried out at 60 Torr and around 55 s^{-1} for those at 15 Torr. Plots of ($k' - k_{dif}$) versus the ester concentrations are shown in Figure 1. In all cases the data show a good linearity. The measured pseudo-first-order rate constant (k') for a particular experiment was obtained from the slope of a ln [Cl] vs t plot. Values for the rate coefficients (k) were then derived from the least-squares fit of the straight lines of ($k' - k_{dif}$) vs [ester] plots. The quoted errors for k are 2σ from the least-squares analysis. Our final results are obtained from the combination of the results obtained at 15 and 60 Torr since no pressure dependence of the rate coefficients was observed in this pressure range, as shown in Table 1. The quoted errors in the final results are 2σ from the statistical analysis and estimated additional uncertainty of 10%.

The only comparison that could be made with previous work is for methyl formate. Using a relative rate technique, Wallington et al. reported a value for the rate coefficient, $k_1 = (1.4 \pm 0.1) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.[16] This value is ca. 25% lower than the result obtained in this work. To our knowledge, there are no other published data for the reactions of Cl atoms with the other esters.

These data first show a much lower reactivity of $HC(O)OCH_3$ ($k_1 = 1.83 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) and $CH_3C(O)OCH_3$ ($k_5 = 2.85 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) compared to the other esters for which the rate constants range from 1.34×10^{-11} ($HC(O)OCH_2CH_3$) to 2.73×10^{-10} cm^3 $molecule^{-1}$ s^{-1} ($C_5H_{11}C(O)OCH_3$). The lowest rate constants are obtained for

TABLE 1: Summary of Experimental Conditions and the Obtained Rate Coefficients for the Reaction of Cl with Esters at Room Temperature

molecule	P (Torr)	no. of runs	[ester] (10^{12} molecule cm^{-3})	$k' - k_{dif}$ (s^{-1})	$(k \pm 2\sigma)^a$ (cm^3 molecule^{-1} s^{-1})
$HC(O)OCH_3$ (methyl formate)	15	6	(112−428)	(234−804)	$(1.90 \pm 0.08) \times 10^{-12}$
	60	16	(74−657)	(171−1185)	$(1.82 \pm 0.03) \times 10^{-12}$
					$k_1 = (1.83 \pm 0.21) \times 10^{-12}$
$HC(O)OCH_2CH_3$ (ethyl formate)	15	5	(93−353)	(1254−4794)	$(1.37 \pm 0.03) \times 10^{-11}$
	60	13	(61−589)	(840−7692)	$(1.33 \pm 0.03) \times 10^{-11}$
					$k_2 = (1.34 \pm 0.15) \times 10^{-11}$
$HC(O)O(CH_2)_2CH_3$ (*n*-propyl formate)	15	6	(26−97)	(1610−5697)	$(5.87 \pm 0.09) \times 10^{-11}$
	60	13	(15−147)	(850−8319)	$(5.58 \pm 0.09) \times 10^{-11}$
					$k_3 = (5.63 \pm 0.65) \times 10^{-11}$
$HC(O)O(CH_2)_3CH_3$ (*n*-butyl formate)	15	5	(6−31)	(754−4391)	$(1.40 \pm 0.04) \times 10^{-10}$
	60	12	(9−57)	(1081−8071)	$(1.41 \pm 0.03) \times 10^{-10}$
					$k_4 = (1.41 \pm 0.17) \times 10^{-10}$
$CH_3C(O)OCH_3$ (methyl acetate)	15	7	(65−294)	(213−885)	$(3.00 \pm 0.10) \times 10^{-12}$
	60	15	(33−372)	(99−1042)	$(2.79 \pm 0.05) \times 10^{-12}$
					$k_5 = (2.85 \pm 0.35) \times 10^{-12}$
$CH_3C(O)OCH_2CH_3$ (ethyl acetate)	15	6	(21−78)	(461−1626)	$(2.11 \pm 0.05) \times 10^{-11}$
	60	12	(19−196)	(405−3763)	$(1.99 \pm 0.06) \times 10^{-11}$
					$k_6 = (2.01 \pm 0.25) \times 10^{-11}$
$CH_3C(O)O(CH_2)_2CH_3$ (*n*-propyl acetate)	15	5	(3−18)	(283−1344)	$(7.91 \pm 0.31) \times 10^{-11}$
	60	12	(5−32)	(412−2421)	$(7.73 \pm 0.15) \times 10^{-11}$
					$k_7 = (7.76 \pm 0.92) \times 10^{-11}$
$CH_3C(O)O(CH_2)_3CH_3$ (*n*-butyl acetate)	15	6	(2−7)	(438−1274)	$(1.81 \pm 0.03) \times 10^{-10}$
	60	13	(2−15)	(473−2556)	$(1.73 \pm 0.04) \times 10^{-10}$
					$k_8 = (1.74 \pm 0.20) \times 10^{-10}$
$CH_3C(O)OCH(CH_3)_2$ (isopropyl acetate)	15	6	(6−28)	(201−745)	$(2.72 \pm 0.12) \times 10^{-11}$
	60	8	(4−34)	(149−924)	$(2.65 \pm 0.09) \times 10^{-11}$
					$k_9 = (2.68 \pm 0.34) \times 10^{-11}$
$CH_3C(O)OCH_2CH(CH_3)_2$ (isobutyl acetate)	15	5	(3−13)	(424−1314)	$(1.06 \pm 0.03) \times 10^{-10}$
	60	12	(2−17)	(220−1834)	$(1.09 \pm 0.03) \times 10^{-10}$
					$k_{10} = (1.08 \pm 0.13) \times 10^{-10}$
$CH_3C(O)OC(CH_3)_3$ (*tert*-butyl acetate)	15	5	(6−31)	(169−734)	$(2.42 \pm 0.04) \times 10^{-11}$
	60	12	(2−42)	(79−1034)	$(2.42 \pm 0.05) \times 10^{-11}$
					$k_{11} = (2.42 \pm 0.28) \times 10^{-11}$
$CH_3C(O)OCH(CH_3)C_2H_5$ (*sec*-butyl acetate)	15	6	(3−11)	(267−1002)	$(9.25 \pm 0.18) \times 10^{-11}$
	60	11	(2−13)	(229−1194)	$(9.02 \pm 0.14) \times 10^{-11}$
					$k_{12} = (9.1 \pm 1.0) \times 10^{-11}$
$C_2H_5C(O)OCH_3$ (methyl propionate)	15	8	(8−104)	(222−1962)	$(1.96 \pm 0.07) \times 10^{-11}$
	60	8	(9−99)	(295−1905)	$(1.99 \pm 0.08) \times 10^{-11}$
					$k_{13} = (1.98 \pm 0.26) \times 10^{-11}$
$C_3H_7C(O)OCH_3$ (methyl butyrate)	15	15	(2−24)	(229−2071)	$(8.57 \pm 0.16) \times 10^{-11}$
	60	6	(3−41)	(256−3454)	$(8.61 \pm 0.11) \times 10^{-11}$
					$k_{14} = (8.6 \pm 0.9) \times 10^{-11}$
$C_4H_9C(O)OCH_3$ (methyl valerate)	15	6	(2−22)	(515−4012)	$(1.85 \pm 0.04) \times 10^{-10}$
	60	13	(3−38)	(525−6000)	$(1.66 \pm 0.06) \times 10^{-10}$
					$k_{15} = (1.7 \pm 0.2) \times 10^{-10}$
$C_5H_{11}C(O)OCH_3$ (methyl caproate)	15	5	(2−11)	(625−3053)	$(2.69 \pm 0.06) \times 10^{-10}$
	60	8	(3−16)	(843−4334)	$(2.73 \pm 0.07) \times 10^{-10}$
					$k_{16} = (2.72 \pm 0.32) \times 10^{-10}$

[a] The quoted errors in the final results are 2σ from the statistical analysis and estimated additional uncertainty of 10%.

the molecules $HC(O)OCH_3$ and $CH_3C(O)OCH_3$, which contain an only H or carbon group (CH_3) in the α position, i.e., adjacent to the −C(O)O− group. There is a deactivating effect of this group on both H and CH_3. H atom is much less reactive in $HC(O)OCH_3$ than in aldehydes ($k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K for $Cl + CH_3CHO$[25]). CH_3 groups in both $HC(O)OCH_3$ and $CH_3C(O)OCH_3$ are much less reactive than in alkanes ($k = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K for $Cl + C_2H_6$[25]). The present low k_5 value for $CH_3C(O)OCH_3$ confirms the strong deactivating effect of a carbonyl group ($-C{=}O$) on CH_3 in the α position, as already observed with acetone and peroxy acetyl nitrate ($k = ((2.37 \pm 0.12) \times 10^{-12}$,[26] $(1.69 \pm 0.32) \times 10^{-12}$,[15] and $(3.06 \pm 0.37) \times 10^{-12}$ [27] for $Cl + CH_3C(O)CH_3$, and $k < 2 \times 10^{-14}$ for $Cl + CH_3C(O)O_2NO_2$,[25] in units of cm^3 molecule^{-1} s^{-1}). The present result for $CH_3C(O)OCH_3$ also shows the strong deactivating effect of the C(O)O− group on CH_3 in the α position in the ether end of the molecule.

Considering the other studied esters, the obtained rate coefficients increase from methyl formate to *n*-butyl formate, from methyl acetate to *n*-butyl acetate, and from methyl propionate to methyl caproate. Similar increases of the rate coefficient with the number of carbon atoms are also observed for the reactions of Cl with aliphatic alkanes. For such reactions considered as H-atom transfer reactions, structure−reactivity relationships have been established[9] based on the structure−activity relationship (SAR) method developed by Atkinson[28] for H-atom transfer reactions of the OH radical with a large variety of saturated VOCs. In this work, the SAR method has been tentatively applied to the reactions of Cl atoms with the investigated esters. In the SAR (structure−activity relationship) method the calculation of the overall rate constant is based on the estimation of $-CH_3$, $-CH_2-$, and $>CH-$ group rate constants. These group rate constants depend only on the identity of the substituents bonded to these groups (e.g., in α position): $k(CH_3-X) = k_{prim}F(X)$; $k(X-CH_2-Y) = k_{sec}F(X)$-

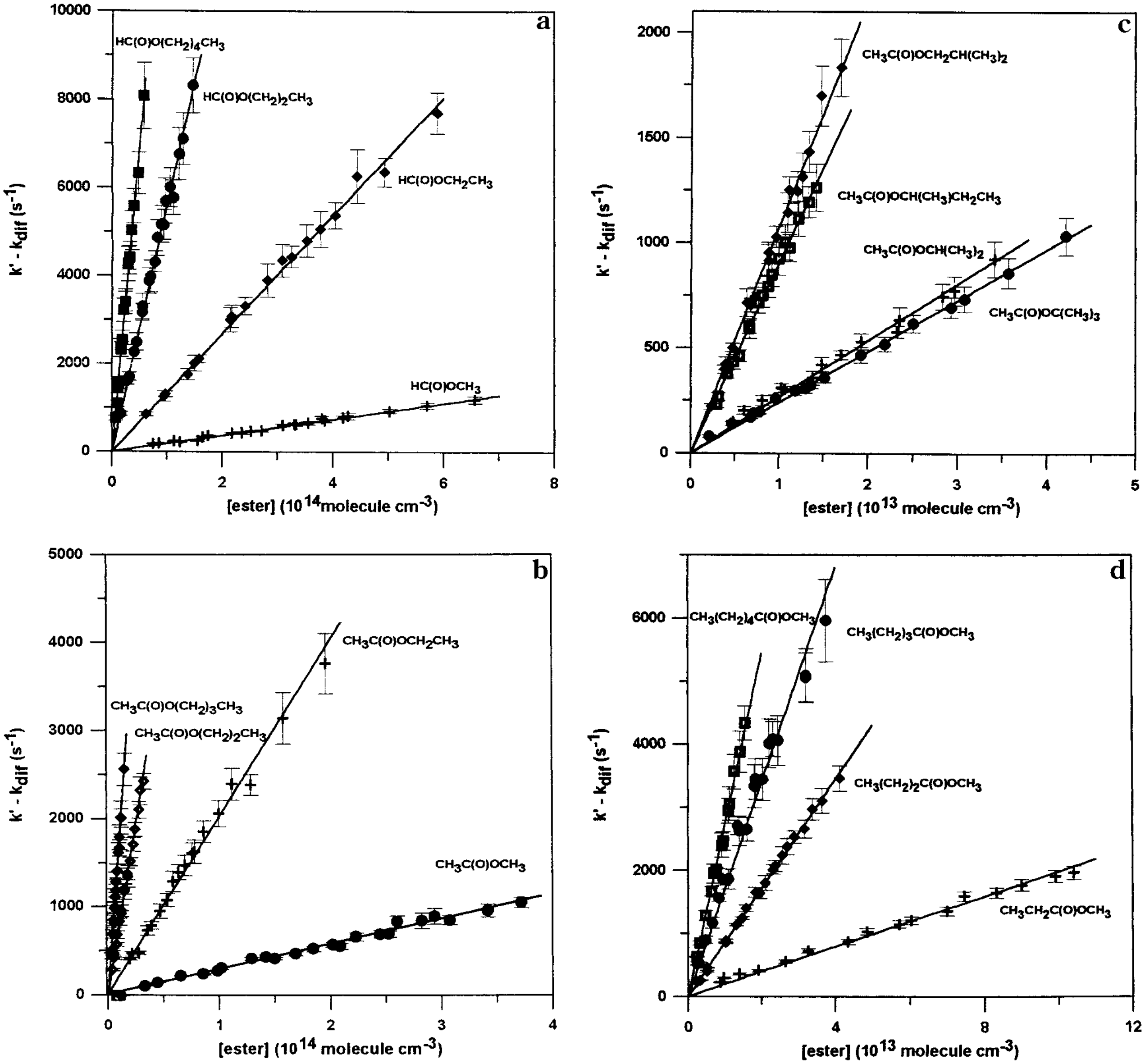

Figure 1. Plots of ($k' - k_{dif}$) vs ester concentration at room temperature. The lines represent the linear least-squares fitting.

F(Y); k(X−CH(Y)(Z)) = $k_{tert}F(\mathrm{X})F(\mathrm{Y})F(\mathrm{Z})$. These parameters deduced from the existing kinetic database for alkanes are the following at 298 K:[9] $k_{prim} = 3.32 \times 10^{-11}$, $k_{sec} = 8.34 \times 10^{-11}$, $k_{tert} = 6.09 \times 10^{-11}$ (in units of cm^3 $molecule^{-1}$ s^{-1}), $F(-CH_3) = 1.00$ and $F(-CH_2-) = F(>CH-) = F(>C<) = 0.79$. These parameters have been used in the present calculations. The additional substituent factors specific of esters have been determined as follows. $F(-CO)$ has been calculated from the rate constant $k(Cl + CH_3C(O)CH_3) = 2.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}: $F(-CO) = k(Cl + CH_3C(O)CH_3)/2k_{prim} = 0.04$; $F(C(O)O-)$ has been derived by applying the SAR to the reaction $Cl + CH_3C(O)OCH_3$ ($k_5 = 2.85 \times 10^{-12}$, this work): $F(C(O)O-) = (k_5 - k_{prim}F(-C(O))/k_{prim}) = 0.05$. It can be noticed that the calculated SAR value of $k_1(Cl + HC(O)OCH_3)$ using $F(C(O)O-) = 0.05$ is in excellent agreement with the experimental k_1 value if a negligible reactivity of the H atom of the acid end of the $HC(O)OCH_3$ molecule is assumed. This assumption seems reasonable and has been made in the SAR calculations for all the studied formates.

The SAR calculated k_1−k_{16} using the above substituent factors $F(-CO)$ and $F(C(O)O-)$ are reported in Table 2, together with experimental values. For formates and acetates, the agreement between calculated and experimental values is reasonable for the largest esters, which have at least one carbon group in the γ position (i.e., adjacent to a group in the β position, which is itself adjacent to a group in the α position). In contrast, for those that have one or several carbon groups only in the β position, the calculated rate constants are significantly higher than the experimental ones. For instance, the k_{calc}/k_{exp} ratios are respectively 2.3, 1.6, and 3.3 for $k_2(HC(O)OC_2H_5)$, $k_6(CH_3C(O)OC_2H_5)$, and $k_{11}(CH_3C(O)OC(CH_3)_3)$. This seems to indicate that the C(O)O− group also has a deactivating effect on the carbon groups in β position, which is not accounted for in the SAR method. The substituent factor $F(C(O)OCH_2-)$ has been derived from k_2 to take into account such an effect: $F(C(O)OCH_2-) = (k_2 - k_{sec}F(C(O)O-)F(-CH_3))/k_{prim} = 0.28$. Assuming that $F(C(O)OCH_2-) = F(C(O)OCH<) = F(C(O)OC<)$ the rate constants k_2−k_4 for formates and k_6−k_{12} have been calculated by using this substituent factor instead of $F(-CH_2-) = F(>CH-) = F(>C<) = 0.79$ of the SAR method. The calculated rate constants reported in Table 2 show a better agreement between calculated and experimental values for $k_2(HC(O)OC_2H_5)$ indeed, but also for $k_3(HC(O)O(CH_2)_2CH_3)$, $k_9(CH_3C(O)OCH(CH_3)_2)$, and $k_{11}(CH_3C(O)OC(CH_3)_3)$.

TABLE 2: Rate Coefficients for Reactions of Cl Atoms with the Studied Esters: Comparison of the Experimental Values and the Calculated Ones Using SAR Relationships

molecule	reaction no.	k_{exp}[a]	k_{calc}[a,b]	k_{calc}[a,c,d]
$HC(O)OCH_3$	1	1.83×10^{-12}	1.66×10^{-12}	1.66×10^{-12}
$HC(O)OCH_2CH_3$	2	1.34×10^{-11}	3.04×10^{-11}	1.35×10^{-11}
$HC(O)O(CH_2)_2CH_3$	3	5.63×10^{-11}	9.63×10^{-11}	5.29×10^{-11}
$HC(O)O(CH_2)_3CH_3$	4	1.41×10^{-10}	1.48×10^{-10}	1.14×10^{-10}
$CH_3C(O)OCH_3$	5	2.85×10^{-12}	2.99×10^{-12}	2.99×10^{-12}
$CH_3C(O)OCH_2CH_3$	6	2.01×10^{-11}	3.17×10^{-11}	1.48×10^{-11}
$CH_3C(O)O(CH_2)_2CH_3$	7	7.76×10^{-11}	9.76×10^{-11}	5.42×10^{-11}
$CH_3C(O)O(CH_2)_3CH_3$	8	1.74×10^{-10}	1.50×10^{-10}	1.15×10^{-10}
$CH_3C(O)OCH(CH_3)_2$	9	2.68×10^{-11}	5.68×10^{-11}	2.30×10^{-11}
$CH_3C(O)OCH_2CH(CH_3)_2$	10	1.08×10^{-10}	1.04×10^{-10}	0.74×10^{-10}
$CH_3C(O)OC(CH_3)_3$	11	2.42×10^{-11}	8.00×10^{-11}	2.92×10^{-11}
$CH_3C(O)OCH(CH_3)C_2H_5$	12	9.08×10^{-11}	1.22×10^{-10}	5.33×10^{-11}
$C_2H_5C(O)OCH_3$	13	1.98×10^{-11}	3.12×10^{-11}	2.03×10^{-11}
$C_3H_7C(O)OCH_3$	14	8.60×10^{-11}	9.64×10^{-11}	6.90×10^{-11}
$C_4H_9C(O)OCH_3$	15	1.70×10^{-10}	1.48×10^{-10}	1.27×10^{-10}
$C_5H_{11}C(O)OCH_3$	16	2.72×10^{-10}	2.0×10^{-10}	1.79×10^{-10}

[a] In units of cm^3 molecule^{-1} s^{-1}. [b] k_{prim}, k_{sec}, k_{tert}, and the substituent factors $F(-CH_3)$, $F(-CH_2-)$, $F(>CH-)$, and $F(>C<)$ are from ref 9; $F(-CO)$ and $F(C(O)O-)$ are from this work (see text). [c] Same as *b* except that the deactivating effect of the $(-C(O)O-)$ group on the CH_x ($x = 0, 1, 2, 3$) groups in the β position have been considered (see text). [d] For methyl esters same as *a* except $F(-CH_2C(O)O) = 0.46$ instead of $F(-CH_2-) = 0.79$.

TABLE 3: Rate Coefficients for the Reactions of Cl Atoms with Esters Determined in This Work at Room Temperature Compared with the Rate Coefficients for the Reactions of OH Radicals with the Same Esters[29-32]

ester	reaction no.	$k_{(OH)}$(10^{-12} cm^3 molecule^{-1} s^{-1}) [ref]	$k_{(Cl)}$(10^{-12} cm^3 molecule^{-1} s^{-1})
$HC(O)OCH_3$	1	0.173 [29]	1.83
$HC(O)OCH_2CH_3$	2	0.852 [29]	13.4
$HC(O)O(CH_2)_2CH_3$	3	1.8 [29]	56.3
$HC(O)O(CH_2)_3CH_3$	4	3.54 [29]	141
$CH_3C(O)OCH_3$	5	0.32 [30]	2.85
$CH_3C(O)OCH_2CH_3$	6	1.67 [30]	20.1
$CH_3C(O)O(CH_2)_2CH_3$	7	3.42 [30]	77.6
$CH_3C(O)O(CH_2)_3CH_3$	8	5.52 [30]	174
$CH_3C(O)OCH(CH_3)_2$	9	3.77 [31]	26.8
$CH_3C(O)OCH_2CH(CH_3)_2$	10	6.33 [31]	108
$CH_3C(O)OC(CH_3)_3$	11	0.56 [31]	24.2
$CH_3C(O)OCH(CH_3)C_2H_5$	12	6.04 [31]	90.8
$CH_3CH_2C(O)OCH_3$	13	0.83 [32]	19.8
$CH_3(CH_2)_2C(O)OCH_3$	14	3.30 [32]	86
$CH_3(CH_2)_3C(O)OCH_3$	15	4.83 [32]	170
$CH_3(CH_2)_4C(O)OCH_3$	16	7.15 [32]	272

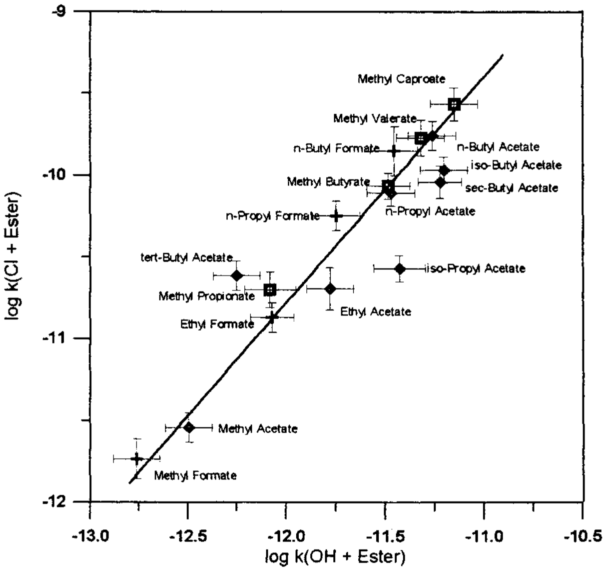

Figure 2. Free energy plots log(*k*(Cl + ester)) vs log(*k*(OH + ester)) for the reactions of Cl and OH with the studied esters. The rate constants for the Cl reactions are from this work, those from the OH reactions are from refs 29−32.

For the largest esters the calculated values are somewhat lower than the experimental ones. Then, a more extended database is required for Cl + formates and acetates reactions before concluding about the existence of a deactivating effect of the C(O)O− group on the carbon groups in the β position in the esters, which is suggested in this paper.

For the methyl esters, similar calculations have been carried out (Table 2). The SAR calculation gives results in fair agreement with the experimental data, even if for $k_{13}(C_2H_5C(O)OCH_3)$, experimental and calculated values are better fitted by considering a deactivating effect of $-C(O)O$ on the CH_3 group in the β position (the fit is obtained for $F(-CH_2C(O)OCH_3) = 0.46$). The calculated rate constants using this substituent factor instead of $F(-CH_2) = 0.79$ gives similar agreement with experimental values for $k_{14}(C_3H_7C(O)OCH_3)$ but poorer agreement for $k_{15}(C_4H_9C(O)OCH_3)$ and $k_{16}(C_5H_{11}C(O)OCH_3)$.

The reactivity of Cl atoms with the studied esters can be compared with the reactivity of OH radicals with the same esters. As can be seen in Table 3, the Cl and OH reaction rate coefficients show similar trends with the number of carbon atoms and the branching in the esters as was reported by Aschmann and Atkinson for Cl and OH reactions with alkanes.[9] The free energy plots for the studied esters, log(*k*(Cl + ester)) vs log(*k*(OH + ester)) are reported in Figure 2. It can be shown that there is a linear correlation for formates and linear acetates but not for the nonlinear acetates. An unweighted least-squares analysis of the data for the formates and linear acetates yields the equation log(*k*(Cl + ester)) = (1.39 ± 0.15)log(*k*(OH + ester)) + (5.86 ± 1.80)

This correlation may be used to estimate the reactivities at room temperature of the aliphatic esters toward Cl atoms from the corresponding reactivities toward OH radicals within less than 50%.

Concerning the atmospheric implication of the present work, the Cl + ester reaction rates have to be compared with that of the OH + ester reaction. The reactions of Cl with esters have high rate constants (in the range 2×10^{-12}– 3×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K) and the rate constant ratio for the reactions of esters with Cl atoms and OH radicals is in the range, $k_{Cl}/k_{OH} \sim 7-43$. But, considering typical tropospheric concentrations of Cl and OH of 1×10^3 and 1×10^6 molecule cm^{-3}, respectively (i.e., $[Cl]/[OH] = 10^{-3}$), the Cl reaction is a negligible loss process of the esters compared to the OH reaction. The Cl reaction would become a significant loss process for the esters only in areas where higher [Cl]/[OH] concentration ratios could be found (average [Cl]/[OH] ratio up to 10^{-1} has been estimated all over the morning in the surface layer of the North Atlantic[33]).

References and Notes

(1) Atkinson, R. *J. Phys. Chem. Ref. Data, Monograph No. 2* **1994**.

(2) Jobson, B. J.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. *J. Geophys. Res.* **1992**, *99*, 25355.

(3) Pszenny, A. A. P.; Keene, W. C.; Jacob, D. J.; Fan, S.; Maben, J. R.; Zetwo, M. P.; Springer-Young, M.; Galloway, J. N. *Geophys. Res. Lett.* **1993**, *20*, 699.

(4) Finlayson-Pitts, B. *J. Res. Chem. Intermed.* **1993**, *19*, 235.

(5) Graedel, T. E.; Keene, W. C. *Global Biogeochem. Cycles* **1995**, *9*, 47.

(6) Keene, W. C.; Jacob, D. J.; Fan, S. M. *Atmos. Environ.* **1996**, *30*, 1.

(7) Finlayson-Pitts, B. J. J. *Geophys. Res.* **1993**, *98*, 14991.

(8) Leu, M. T.; Timonen, R. S.; Keyser, L. F.; Yung, Y. T. *J. Phys. Chem.* **1995**, *99*, 13203.

(9) Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1995**, *27*, 613.

(10) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 9788.

(11) Pilgrim, J. S.; Taatjes, C. A. *J. Phys. Chem. A* **1997**, *101*, 5776.

(12) Tyndall, G. S.; Orlando, J. J.; Wallington, T. J.; Dill, M.; Kaiser, E. W. *Int. J. Chem. Kinet.* **1997**, *29*, 43.

(13) Beichert, P.; Wingen, L.; Lee, J.; Vogt, R.; Ezell, M. J.; Ragains, M.; Neavyn, R.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1995**, *99*, 13156.

(14) Notario, A.; Le Bras, G.; Mellouki, A. *Chem. Phys. Lett.* **1998**, *281*, 421.

(15) Olsson, B. O. R.; Hallquist, M.; Ljungström, E.; Davidsson, J. *Int. J. Chem. Kinet.* **1997**, *29*, 195.

(16) Wallington, T. J.; Hurley, M. D., Ball, J. C., Jenkin, M. E. *Chem. Phys. Lett.* **1993**, *211*, 41.

(17) Tuazon, E. C.; Carter, W. P. L.; Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1991**, *23*, 1003.

(18) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1991**, *23*, 907.

(19) Japar, S. M.; Wallington, T. J.; Rudy, S. J.; Chang, T. Y. *Environ. Sci. Technol.* **1991**, *25*, 415.

(20) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int. J. Chem. Kinet.* **1995**, *27*, 453.

(21) Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1992**, *215*, 199.

(22) Mellouki, A. *J. Chim. Phys.* **1998**, *95*, 513.

(23) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1995**, *99*, 8669.

(24) Bilde, M.; Møgelberg, T. E.; Sehested, J.; Nielsen, O. J.; Wallington, T. J.; Hurley, M. D.; Japar, S. M.; Dill, M.; Orkin, V. L.; Buckley, T. J.; Huie, R. E.; Kurylo, M. J. *J. Phys. Chem. A* **1997**, *101*, 3514.

(25) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, Jr. R. F.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, 26.

(26) Wallington, T. J.; Andino, J. M.; Ball, J. C.; Japar, S. M. *J. Atmos. Chem.* **1990**, *10*, 301.

(27) Notario, A.; Le Bras, G.; Mellouki, A., to be submitted.

(28) Kwok, E. S. C.; Atkinson R. *Atmos. Environ.* **1995**, *29*, 1685.

(29) Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem.* **1997**, *101*, 5489.

(30) El Boudali, A.; Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem.* **1996**, *100*, 12364.

(31) Le Calvé, S.; Le Bras, G.; Mellouki, A. *Int. J. Chem. Kinet.* **1997**, *29*, 683.

(32) Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem.* **1997**, *101*, 9137.

(33) Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, Jr. T. W.; Blake, D. R.; Rowland, F. S. *J. Geophys. Res.* **1996**, *101*, 4331.