

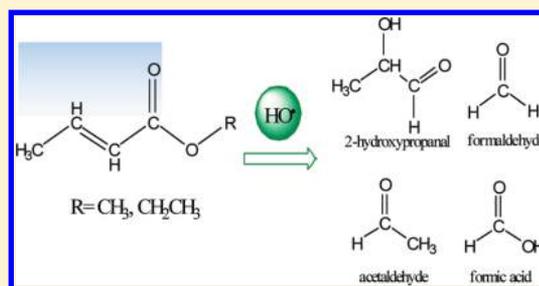
# Gas-Phase Oxidation of Methyl Crotonate and Ethyl Crotonate. Kinetic Study of Their Reactions toward OH Radicals and Cl Atoms

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**ABSTRACT:** Rate coefficients for the reactions of hydroxyl radicals and chlorine atoms with methyl crotonate and ethyl crotonate have been determined at 298 K and atmospheric pressure. The decay of the organics was monitored using gas chromatography with flame ionization detection (GC-FID), and the rate constants were determined using the relative rate method with different reference compounds. Room temperature rate coefficients were found to be (in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ):  $k_1(\text{OH} + \text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3) = (4.65 \pm 0.65) \times 10^{-11}$ ,  $k_2(\text{Cl} + \text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3) = (2.20 \pm 0.55) \times 10^{-10}$ ,  $k_3(\text{OH} + \text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3) = (4.96 \pm 0.61) \times 10^{-11}$ , and  $k_4(\text{Cl} + \text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3) = (2.52 \pm 0.62) \times 10^{-10}$  with uncertainties representing  $\pm 2\sigma$ . This is the first determination of  $k_1$ ,  $k_3$ , and  $k_4$  under atmospheric pressure. The rate coefficients are compared with previous determinations for other unsaturated and oxygenated VOCs and reactivity trends are presented. In addition, a comparison between the experimentally determined  $k_{\text{OH}}$  with  $k_{\text{OH}}$  predicted from  $k$  vs  $E_{\text{HOMO}}$  relationships is presented. On the other hand, product identification under atmospheric conditions has been performed for the first time for these unsaturated esters by the GC-MS technique in  $\text{NO}_x$ -free conditions. 2-Hydroxypropanal, acetaldehyde, formaldehyde, and formic acid were positively observed as degradation products in agreement with the addition of OH to C2 and C3 of the double bond, followed by decomposition of the 2,3- or 3,2-hydroxyalkoxy radicals formed. Atmospheric lifetimes, based on of the homogeneous sinks of the unsaturated esters studied, are estimated from the kinetic data obtained in the present work.



## INTRODUCTION

$\alpha,\beta$ -Unsaturated VOCs are emitted to the atmosphere from biogenic and anthropogenic sources including the polymer industry. Limited information is found on the atmospheric degradation of unsaturated carbonyl compounds, most of which are estimations of the rate constants using structure activity relationships (SARs).<sup>1–3</sup>

Particularly, unsaturated esters containing a double bond and functional carboxyl group are mainly emitted to the atmosphere for their use as monomers or comonomers in making acrylic and modacrylic fibers. They are used in formulating paints and dispersions for paints, inks and adhesives, in making cleaning products, antioxidant agents, and amphoteric surfactants as well as in making aqueous resins and dispersions for textiles and papers.<sup>4–6</sup>

Methyl and ethyl crotonate are used in industry as precursors of aromatic bases in cosmetics, shampoos, soaps, detergents, and cleaning agents.<sup>7</sup>

Once in the atmosphere, the esters can be degraded by the photoxidation initiated by OH and  $\text{NO}_3$  radicals,  $\text{O}_3$  molecules or Cl atoms together with physical processes like wet and dry deposition or photolysis. Therefore, it is necessary to obtain experimental kinetic information of their reactions with main tropospheric oxidants, so as to calculate their residence times in the atmosphere and assess their impact on the air quality.

The formation of low-vapor pressure organic compounds, like carboxylic acids, may also contribute to the formation of nuclei of condensation leading particle production.<sup>1,8</sup>

In this work we report room temperature atmospheric pressure measurements of rate coefficients for the reactions of OH radicals and Cl atoms with methyl crotonate and ethyl crotonate:



Experiments were performed using a collapsible Teflon chamber at room temperature and atmospheric pressure by the relative rate method with different reference compounds.

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Reaction 2 was previously studied only in a recent work at 298 K and 760 Torr by the relative rate technique in a 1080 L photoreactor coupled with FTIR detection of the organics.<sup>9</sup>

To the best of our knowledge, the rate coefficients for the reactions of OH radicals with methyl crotonate and ethyl crotonate and for the reaction of Cl atoms with ethyl crotonate have not been reported previously in the literature. Therefore, this is the first determination of the rate constants for the reactions 1, 3, and 4.

In conjunction with other available kinetic data, the results are discussed in terms of the substituent effects on the reactivity of the olefinic carbons. The rate coefficients obtained in this work, together with other values from literature for similar unsaturated and oxygenated VOCs, were compared to obtain reactivity trends that compute the effect of substituents on reactivity of the  $\alpha,\beta$ -unsaturated VOC.

On the other hand, the kinetic data obtained in this work for the OH reactions are compared with the calculated values from our previous correlation between the reactivity of the unsaturated compounds toward OH radicals with the  $E_{\text{HOMO}}$  (energy of the highest occupied molecular orbital) of the unsaturated compounds.

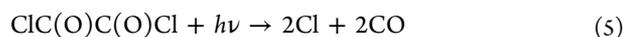
In addition, product studies using the GC–MS technique under atmospheric conditions were carried out for the first time for these unsaturated esters. The information was used to postulate a general reaction mechanism and the most favored channel of the OH-initiated degradation of crotonates in the gas phase and in the atmosphere.

Atmospheric lifetimes of the esters studied in this work were calculated taking into account the experimental rate constants obtained.

## EXPERIMENTAL SECTION

All experiments were performed in an 80 L Teflon bag located in a wooden box with the internal walls covered by aluminum foil.

Cl atoms were generated by UV photolysis of oxalyl chloride (ClC(O)C(O)Cl):



OH radicals were generated by UV irradiation of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ):



Four germicidal lamps (Philips 30W) were used for the generation of OH radical and Cl atoms.

Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in  $\text{N}_2$  or pure air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of zero grade  $\text{N}_2$  or synthetic air and the bag was then filled with the zero grade  $\text{N}_2$  or synthetic air. Before each set of experiments, the Teflon bag was cleaned by being filled with a mixture of  $\text{O}_2$  and  $\text{N}_2$  photolyzed for 15–25 min using 4 germicidal lamps (Philips 30W) with a UV emission at 254 nm, to produce  $\text{O}_3$ . After this procedure, the bag was cleaned again by repeated flushing with  $\text{N}_2$ ; before performing the experiments it was checked through gas chromatography that no observable impurities were found.

Periodically, gas samples were removed from the Teflon bag using calibrated Hamilton gas syringes. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak

Q column (Alltech, 2.3 m) held between 170 and 240 °C for reactions 1 and 3 and between 170 and 185 °C for reactions 2 and 4.

In the presence of the oxidant X (Cl atom or OH radical), the reactant and reference compounds decay through the following reactions:



Provided that the reactant and reference compounds are lost only by reactions 7 and 8, then it can be shown that

$$\ln\left\{\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right\} = \frac{k_7}{k_8} \ln\left\{\frac{[\text{reference}]_0}{[\text{reference}]_t}\right\} \quad (1)$$

where  $[\text{reactant}]_0$ ,  $[\text{reference}]_0$ ,  $[\text{reactant}]_t$ , and  $[\text{reference}]_t$  are the concentrations of the reactant and reference compound at times  $t = 0$  and  $t$ , respectively, and  $k_7$  and  $k_8$  are the rate constants of reactions 7 and 8, respectively.

The relative rate technique relies on the assumption that the reactant and reference organics are removed solely by reaction with the oxidant species X (Cl or OH). To verify this assumption, mixtures of oxalyl chloride or hydrogen peroxide and air or nitrogen with both organics were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the precursor of X, in the absence of UV light, was of negligible importance over the typical time periods used in this work. Additionally, to test for possible photolysis of the reactants used, mixtures of the reactants in nitrogen or air in the absence of oxalyl chloride or hydrogen peroxide were irradiated for 30 min using the output of all the germicidal lamps surrounding the chamber. No photolysis of any of the reactants was observed.

The initial concentrations used in the experiments for the determination of the rate constant of reactions 1–4 were in the range 60–250 ppm (1 ppm =  $2.46 \times 10^{13}$  molecules  $\text{cm}^{-3}$  at 298 K and 760 Torr of total pressure) for crotonates and 180–270 ppm for  $(\text{CH}_3\text{CH}_2)_2\text{O}$ ,  $\text{CH}_2=\text{CHCH}_2\text{Cl}$  and  $\text{CH}_2=\text{CHCN}$ , used as reference compounds. The concentration of ClC(O)C(O)Cl ranged from 40 to 120 ppm and for  $\text{H}_2\text{O}_2$  from 50 to 130 ppm in around 750 Torr of either  $\text{N}_2$  or synthetic air.

The analytical technique employed for qualitative identification of the products formed after irradiation was terminated was GC–mass spectrometry on a Shimadzu GC–MS QP 5050 spectrometer equipped with a 30 m to 0.12 mm DB-5 MS column.

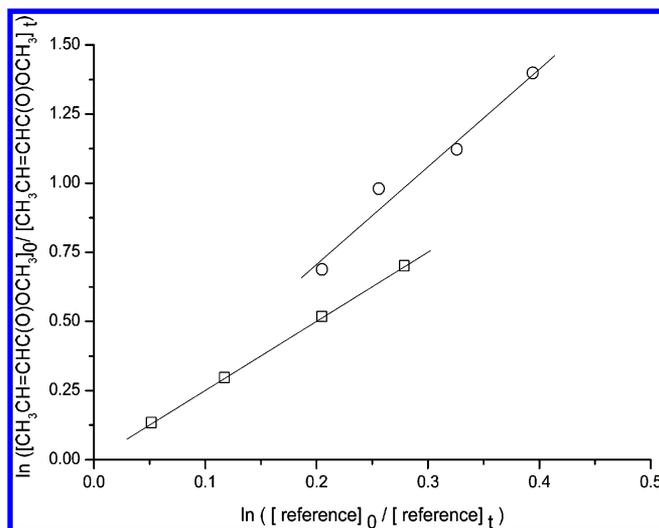
## MATERIALS

The chemicals used were  $\text{N}_2$  (AGA, 99.999%), synthetic air (AGA, 99.999%), methyl crotonate (Fluka, 99%), ethyl crotonate (Fluka, 99%) diethyl ether (Fluka, 99%), 3-chloropropene (Fluka, 98%), acrylonitrile (Baker, 99.5%),  $\text{H}_2\text{O}_2$  (Cicarelli 60% wt), and ClC(O)C(O)Cl (Aldrich, 98%). The organics were degassed by repeated freeze–pump–thaw cycling.

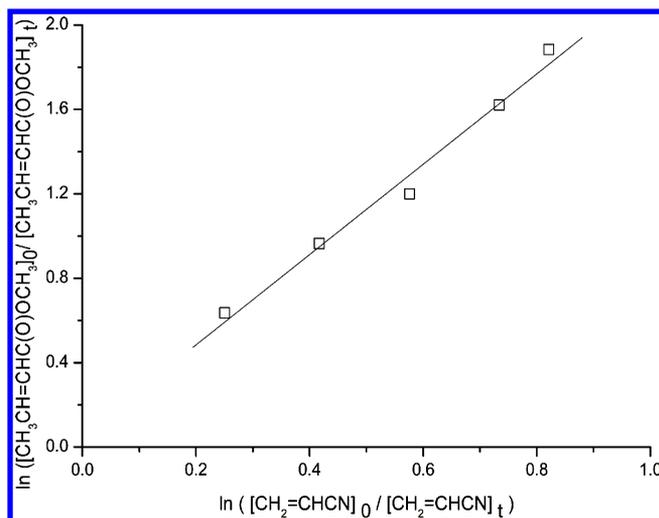
## RESULTS

By using the relative rate technique, we obtained from eq 1 the rate constants for the four reactions studied. The data were fitted to a straight line by the linear least-squares procedure.

Figures 1–4 show the losses of methyl crotonate and ethyl crotonate by their reactions with OH radicals and Cl atoms, in the presence of different reference compounds.



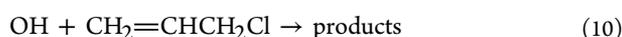
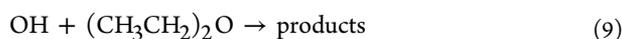
**Figure 1.** Plots of the kinetic data for the reaction of methyl crotonate with OH radicals using 3-chloropropene ( $\square$ ) and diethyl ether ( $\circ$ ) as reference hydrocarbons determined at 298 K and atmospheric pressure of synthetic air.



**Figure 2.** Plot of the kinetic data for the reaction of methyl crotonate with Cl atoms using acrylonitrile as reference hydrocarbon, determined at 298 K and atmospheric pressure of synthetic air.

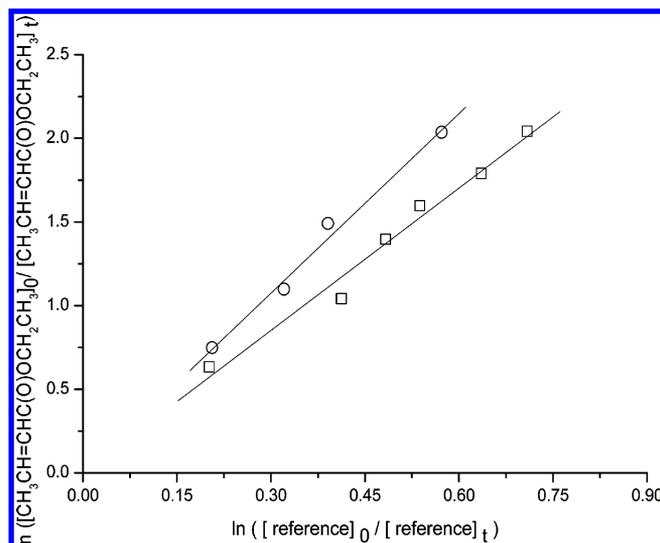
For the sake of clarity, only one example of the rate constant determination is presented in Figures 1–4.

The following were used as reference reactions to determine the rate coefficient of reactions 1–4:

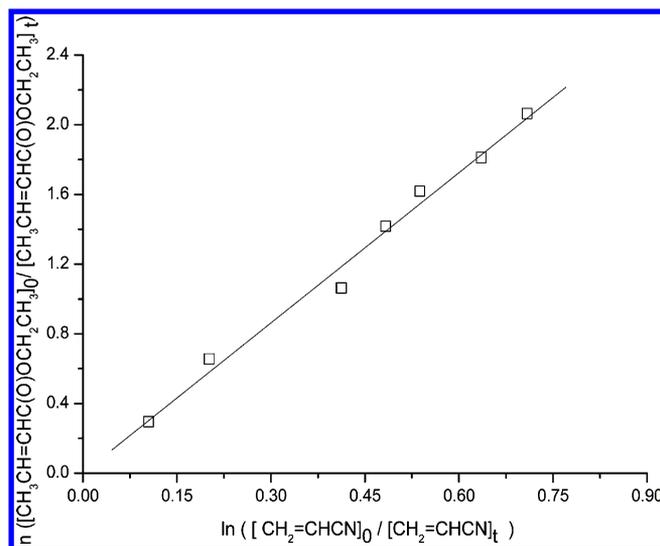


where  $k_9 = (1.36 \pm 0.11) \times 10^{-11,10}$ ,  $k_{10} = (1.69 \pm 0.07) \times 10^{-11,11}$  and  $k_{11} = (1.11 \pm 0.23) \times 10^{-10,12}$ . All the  $k$  values are in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Table 1 displays the data on relative rate constants  $k_{\text{reactant}}/k_{\text{reference}}$  and absolute rate constants  $k_{\text{reactant}}$  at room temperature (298 K). The ratios were obtained from the average of several experiments using different initial concentrations of the reactants.



**Figure 3.** Plots of the kinetic data for the reaction of ethyl crotonate with OH radicals using 3-chloropropene ( $\square$ ) and diethyl ether ( $\circ$ ) as reference hydrocarbons, determined at 298 K and atmospheric pressure of synthetic air.



**Figure 4.** Plot of the kinetic data for the reaction of ethyl crotonate with Cl atoms using acrylonitrile as reference hydrocarbon, determined at 298 K and atmospheric pressure of synthetic air.

The rate constants obtained by averaging the values from different experiments were the following:

$$k_1 = (4.65 \pm 0.65) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (2.20 \pm 0.55) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (4.96 \pm 0.61) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_4 = (2.52 \pm 0.62) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, from which we have considered also the corresponding error on the reference rate constants.

As can be observed in Table 1, the experiments for the reaction 3 using 3-chloropropene as a reference, were performed in  $\text{N}_2$

**Table 1.** Rate Constant Ratio  $k_{\text{reactant}}/k_{\text{reference}}$  and Rate Constants for the Reactions of OH Radicals and Cl Atoms with Methyl Crotonate and Ethyl Crotonate at  $298 \pm 2$  K in  $760 \pm 10$  Torr of Air (Marked with Asterisk) or Nitrogen

reaction	ref	$k_{\text{reactant}}/k_{\text{reference}}$	$k_{\text{reactant}}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3 + \text{OH}$	3-chloropropene	$2.51 \pm 0.09$	$(4.24 \pm 0.33) \times 10^{-11}$
	3-chloropropene	$2.50 \pm 0.11$	$(4.23 \pm 0.36) \times 10^{-11}$
	diethyl ether	$3.53 \pm 0.15$	$(4.80 \pm 0.59) \times 10^{-11}$
	diethyl ether	$3.93 \pm 0.16$	$(5.34 \pm 0.65) \times 10^{-11}$
	average		$(4.65 \pm 0.65) \times 10^{-11}$
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3 + \text{Cl}$	acrylonitrile	$1.81 \pm 0.09$	$(2.01 \pm 0.52) \times 10^{-10}$
	acrylonitrile	$2.14 \pm 0.05$	$(2.38 \pm 0.55) \times 10^{-10}$
	average		$(2.20 \pm 0.55) \times 10^{-10}$
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3 + \text{OH}$	3-chloropropene*	$2.98 \pm 0.15$	$(5.04 \pm 0.46) \times 10^{-11}$
	3-chloropropene	$2.84 \pm 0.12$	$(4.80 \pm 0.40) \times 10^{-11}$
	diethyl ether	$3.58 \pm 0.14$	$(4.87 \pm 0.58) \times 10^{-11}$
	diethyl ether	$3.78 \pm 0.14$	$(5.14 \pm 0.61) \times 10^{-11}$
	average		$(4.96 \pm 0.61) \times 10^{-11}$
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3 + \text{Cl}$	acrylonitrile	$2.55 \pm 0.03$	$(2.83 \pm 0.62) \times 10^{-10}$
	acrylonitrile	$1.99 \pm 0.04$	$(2.21 \pm 0.50) \times 10^{-10}$
	average		$(2.52 \pm 0.62) \times 10^{-10}$

and in the presence of  $\text{O}_2$  using synthetic air to test for potential systematic errors due to secondary reactions, and to obtain a better approach to atmospheric conditions. The fact that the two bath gases produce identical results provides strong evidence of success in minimizing secondary reactions in the chamber. This observation, the linearity of the data points, and the fact that the plots show practically zero intercepts, suggest that the contribution of the secondary reactions with the products of the reactions studied here could be considered negligible.

Further experiments were also conducted to identify reaction products under conditions similar to those of the kinetic experiments for the reactions 1 and 3.

2-Hydroxypropanal ( $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{H}$ ), acetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{H}$ ), formic acid ( $\text{HC}(\text{O})\text{OH}$ ), and formaldehyde ( $\text{HC}(\text{O})\text{H}$ ) were positively identified as reaction products for the reactions of OH radicals with methyl crotonate and ethyl crotonate.

## DISCUSSION

**Comparison with Literature.** For the reaction of Cl atoms with methyl crotonate (reaction 2), our value of  $k_2 = (2.20 \pm 0.55) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is, within the experimental error, in a very good agreement with a recently reported value of  $k_2 = (2.04 \pm 0.56) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in a  $1080 \text{ dm}^3$  quartz-glass reaction chamber at atmospheric pressure with “in situ” FTIR spectroscopy to monitor the organics.<sup>9</sup>

To the best of our knowledge, there are no other prior reported values of the rate constants for the reactions of OH radicals with methyl and ethyl crotonate and for the reaction of Cl atoms with ethyl crotonate. The present study, thus, is the first kinetic study of these reactions; therefore, no direct comparison with the literature can be made. Although, it is interesting to compare the reactivity of the esters studied in this work with that of similar esters and other unsaturated OVOCs from literature.

**Reactivity Trends.** The rate coefficients for the reactions of OH radicals with the crotonates reported in this work are in the same order of magnitude of the rate coefficients reported for the reactions of OH with other unsaturated esters or other oxygenated and unsaturated VOCs (on the order of  $(1-5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).<sup>13-17</sup> However, the position of the double bond in the unsaturated esters and its substituent have distinct effects on the reactivity of the esters toward OH

radicals. To aid the discussion, Table 2 shows averaged values of rate coefficients for the reaction of OH with unsaturated esters reported in this study and in the literature.

**Table 2.** Comparison of the Rate Constants of the Reactions of Different Unsaturated Esters with OH Radicals and Cl Atoms under Atmospheric Pressure at 298 K

ester	$k_{\text{OH}} \times 10^{11}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_{\text{Cl}} \times 10^{10}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
$\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$	$(1.3 \pm 0.2)^a$	$(2.04 \pm 0.54)^d$
$\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$	$(1.7 \pm 0.4)^a$	$(2.53 \pm 0.46)^e$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$	$(4.2 \pm 1.1)^a$	$(2.82 \pm 0.93)^d$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$	$(4.58 \pm 0.59)^b$	$(2.71 \pm 0.21)^f$
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$	$(4.65 \pm 0.65)^c$	$(2.20 \pm 0.55)^c$
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$	$(4.96 \pm 0.61)^c$	$(2.52 \pm 0.62)^c$

<sup>a</sup>From ref 14. <sup>b</sup>From ref 15. <sup>c</sup>This work. <sup>d</sup>From ref 18. <sup>e</sup>From ref 3. <sup>f</sup>From ref 19.

H-substitution by electron donor groups like  $-\text{CH}_3$  or other alkyl groups in the  $\alpha,\beta$ -unsaturated ester increases quite significantly the reactivity of the compounds toward the electrophilic attack of OH radicals. This can be seen from the higher reactivity of methyl methacrylate ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$ ) toward OH radical attack  $k = (4.2 \pm 1.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>14</sup> compared with the value of  $k = (1.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined for the reaction of OH with methyl acrylate ( $\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$ ) reported by Teruel et al.<sup>14</sup> On the other hand, when the H atoms attached to olefinic C1 is substituted by electron donor groups like methyl groups ( $-\text{CH}_3$ ) (see, for example,  $\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$ ), the rate constant increases even more with a value of  $k = (4.65 \pm 0.65) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  compared again with the value of  $k = (1.3 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined for the reaction of OH with methyl acrylate ( $\text{CH}_2=\text{CHC}(\text{O})\text{OCH}_3$ ). The higher reactivity, by the presence of electron-donating substituent, is indicative of an electrophilic addition mechanism; the positive inductive effect of the  $-\text{CH}_3$  group increases the charge density on the double-bonded carbon atom. This enhancement seems to be higher when the  $-\text{CH}_3$  group is attached to the terminal carbon of the double bond increasing the susceptibility of the double bond toward OH radical electrophilic attack.

**$k_{\text{OH}}$  vs  $E_{\text{HOMO}}$  of Crotonates.** Additionally, the rate coefficients obtained for the reactions of methyl crotonate and ethyl crotonate with OH radicals can be compared with values calculated using the recently reported correlation between the reactivity of the unsaturated compounds toward OH radicals with the  $E_{\text{HOMO}}$  of the unsaturated compounds.<sup>18</sup>

The correlation shown in our previous study for different groups of reactions is as follows:

$$\ln k_{\text{OH}}(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -(1.1 \pm 0.2)E_{\text{HOMO}} - (12.6 \pm 1.7) \quad (\text{II})$$

We have calculated the HOMO energies ( $E_{\text{HOMO}}$ ) for the compounds studied (methyl and ethyl crotonate) using the Gaussian 03 package. The geometry optimizations and initial values of energies were obtained at the Hartree–Fock (HF) level, and ab initio Hamiltonian with a 6-31++G(d,p) basis set was used. The values of  $E_{\text{HOMO}}$  obtained were 10.30 eV for methyl crotonate and 10.25 eV for ethyl crotonate, obtaining the following rate coefficients:  $k_{\text{methyl crotonate}+\text{OH}} = 4.05 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_{\text{ethyl crotonate}+\text{OH}} = 4.28 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  through eq II. These values are, within the experimental errors, in very good agreement with the rate coefficient of the reactions 1 and 3 measured in this study of  $(4.65 \pm 0.65) \times 10^{-11}$  and  $(4.96 \pm 0.61) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively.

As observed previously in the reactions of unsaturated esters with Cl atom, the effect of substituents and the chemical structure of the unsaturated compound on the reactivity of the double bond toward Cl atom is less important than the effect observed in

the OH additions.<sup>18</sup> Thus, the rate coefficients for the reactions of Cl atom with different unsaturated compounds (including methyl crotonate and ethyl crotonate) are very similar and agree with one another within the experimental errors (Table 2).

**Product Identification Studies of OH Reactions and Postulated Mechanism.** Product experiments were also performed to identify the reaction products formed for the reactions 1 and 3.

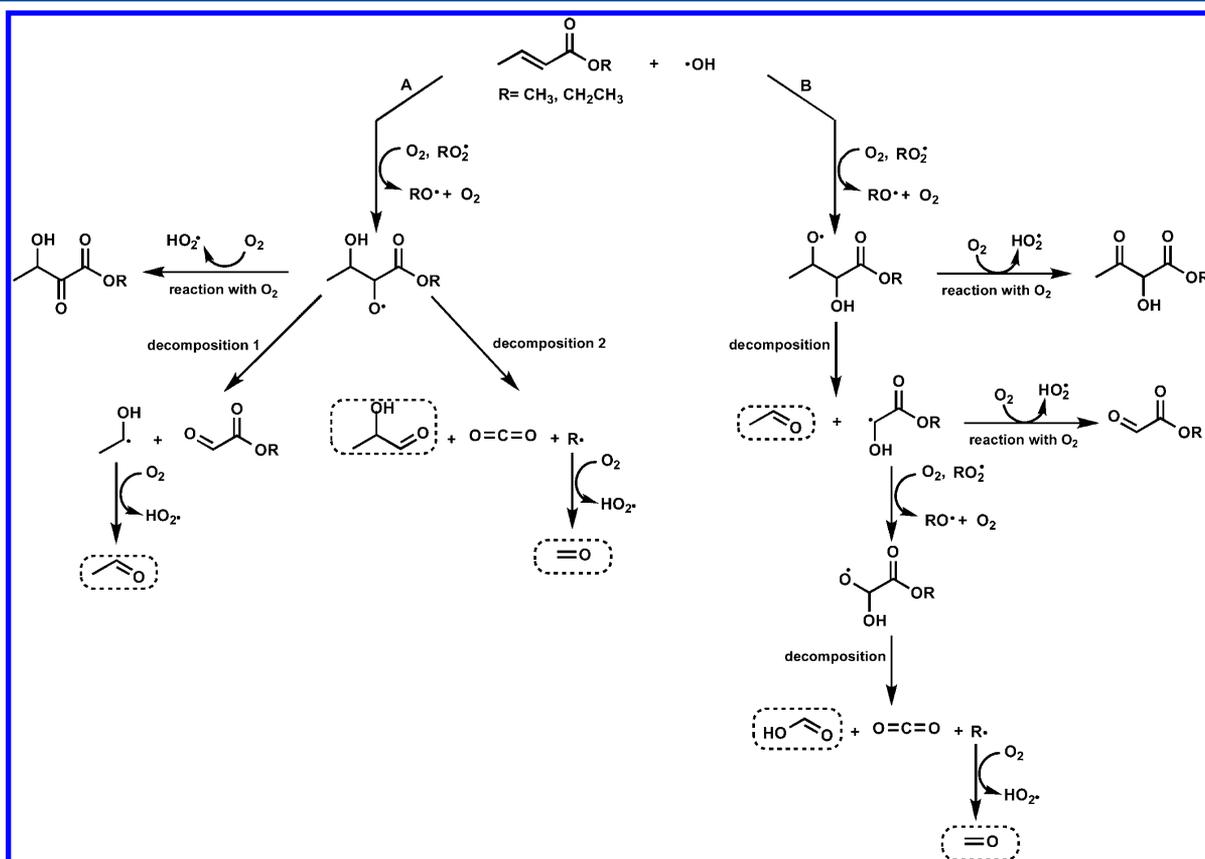
For the reactions of OH radicals with methyl crotonate and ethyl crotonate were positively identified 2-hydroxypropanal, acetaldehyde, formaldehyde, and formic acid as reaction products.

The products found together with the reactivity trends of these compounds,<sup>15,16,20–22</sup> suggest that the reactions of OH radicals with methyl crotonate and ethyl crotonate mainly lead to the formation of hydroxyalkyl radicals by initial addition of OH to the  $>\text{C}=\text{C}<$  double bond. The hydroxyalkyl radicals rapidly react with atmospheric oxygen forming alkyl peroxy radicals. Further, peroxy radicals react with NO or other peroxy radicals (in  $\text{NO}_x$ -free conditions) to give alkoxy radicals.

The alkoxy radicals formed could be  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}^\bullet)\text{C}(\text{O})\text{OCH}_3$  and  $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{CH}(\text{OH})\text{C}(\text{O})\text{OCH}_3$  for the reaction of methyl crotonate + OH and  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}^\bullet)\text{C}(\text{O})\text{OCH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{CH}(\text{OH})\text{C}(\text{O})\text{OCH}_2\text{CH}_3$  for the reaction of ethyl crotonate + OH.

A postulated mechanism for the reactions of OH radicals with methyl crotonate and ethyl crotonate in the absence of  $\text{NO}_x$  is shown in Figure 5.

The addition of OH radicals can be in the C2 forming  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}^\bullet)\text{C}(\text{O})\text{OR}$  (2-hydroxy, 3-alkoxy radicals)



**Figure 5.** Simplified reaction mechanism for the addition channel in the OH-radical initiated oxidation of methyl and ethyl crotonate in the absence of  $\text{NO}_x$ .

(Figure 5, channel A) and/or in the C3 producing  $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{CH}(\text{OH})\text{C}(\text{O})\text{OR}$  (3-hydroxy, 2-alkoxy radicals) (Figure 5, channel B).

For both reactions studied, the 2,3-hydroxyalkoxy radicals formed in the OH radical addition step (Figure 5, channel A) can

- decompose to give methyl glyoxylate ( $\text{HC}(\text{O})\text{C}(\text{O})\text{OCH}_3$ ) or ethyl glyoxylate ( $\text{HC}(\text{O})\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ ) for methyl crotonate and ethyl crotonate reaction, respectively, and acetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{H}$ ) as coproduct (Figure 5A, decomposition 1),
- decompose forming 2-hydroxypropanal ( $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{H}$ ), carbon dioxide and  $\bullet\text{CH}_3$  or  $\bullet\text{CH}_2\text{CH}_3$  radicals for methyl and ethyl crotonate reaction, respectively, with further production of formaldehyde (Figure 5A, decomposition 2), or
- react with  $\text{O}_2$  to form polyfunctional compounds, i.e.,  $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{C}(\text{O})\text{OCH}_3$  or  $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{O})\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ , respectively (Figure 5A, reaction with  $\text{O}_2$ ).

When the OH addition is produced in the C3 of the double bond of the crotonates, the 3-hydroxy, 2-alkoxy radicals formed (Figure 5, channel B) can

- decompose to produce acetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{H}$ ) and  $\bullet\text{CH}(\text{OH})\text{C}(\text{O})\text{OR}$  radicals, which can react further with  $\text{O}_2$  in the presence of  $\text{RO}_2^\bullet$  radicals followed by a decomposition to give formic acid ( $\text{HC}(\text{O})\text{OH}$ ), carbon dioxide, and  $\bullet\text{R}$  radical and further  $\text{CH}_2\text{O}$  production, or  $\bullet\text{CH}(\text{OH})\text{C}(\text{O})\text{OR}$  radicals can react with  $\text{O}_2$  forming methyl glyoxylate ( $\text{HC}(\text{O})\text{C}(\text{O})\text{OCH}_3$ ) or ethyl glyoxylate ( $\text{HC}(\text{O})\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ ) for methyl crotonate and ethyl crotonate reaction, respectively (Figure 5, channel B), or
- react with  $\text{O}_2$  to form  $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{C}(\text{O})\text{OCH}_3$  or  $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{C}(\text{O})\text{OCH}_2\text{CH}_3$ , for methyl crotonate or ethyl crotonate respectively (Figure 5B, reaction with  $\text{O}_2$ ).

In our experimental conditions we observed the presence of 2-hydroxypropanol, which can be formed through channel A and decomposition 2 (Figure 5).

The formation of acetaldehyde and formaldehyde can be explained through the decomposition of the 2-hydroxy, 3-alkoxy radicals and/or 3-hydroxy, 2-alkoxy radicals (Figure 5, channels A and B) and the formic acid found can be formed by the decomposition of the  $\text{CH}_3\text{CH}(\text{O}^\bullet)\text{CH}(\text{OH})\text{C}(\text{O})\text{OR}$  (3-hydroxy, 2-alkoxy radicals) (Figure 5, channel B).

We expected that the main pathway channel in the reactions of OH with methyl and ethyl crotonate could be the OH addition to the less substituted carbon (C2) of the double bond forming 2-hydroxypropanol, acetaldehyde, and formaldehyde (Figure 5, channel A),<sup>23</sup> similar to what was observed by Atkinson for the OH radical addition to alkenes<sup>24,25</sup> and in the OH degradation of other similar unsaturated esters.<sup>22</sup>

Furthermore, the results of recent theoretical calculations performed in our laboratory are in line with the experimental findings obtained in this work.

However, more experimental data (products yields in the presence and in the absence of  $\text{NO}_x$ ) and theoretical calculations using different approaches on the mechanisms probably are needed to have a better understanding and to confirm the degradation chemistry of these non terminal unsaturated esters in the troposphere.

**Atmospheric Implications.** The rate coefficients summarized in Table 1 can be used to estimate the atmospheric lifetimes of the methyl crotonate and ethyl crotonate due to reaction with OH radicals and Cl atoms in comparison to their reactions with the other oxidants like  $\text{O}_3$  and  $\text{NO}_3$  using the expression:  $\tau_x = 1/k_x[X]$  with  $X = \text{OH}, \text{Cl}, \text{O}_3$ , and  $\text{NO}_3$  where  $k_x$  is the rate coefficient for the reaction of the oxidant X with the unsaturated ester and  $[X]$  is the typical atmospheric concentration of the oxidant. For the calculation of lifetimes, the following oxidant concentrations were used:  $[\text{OH}] = 2 \times 10^6$  radicals  $\text{cm}^{-3}$ ,<sup>26</sup>  $[\text{Cl}] = 1 \times 10^4$  atoms  $\text{cm}^{-3}$ ,<sup>27</sup>  $[\text{NO}_3] = 5 \times 10^8$  radicals  $\text{cm}^{-3}$ ,<sup>28</sup> and  $[\text{O}_3] = 7 \times 10^{11}$  molecules  $\text{cm}^{-3}$ .<sup>29</sup>

Table 3 displays the tropospheric lifetimes estimated at 298 K of the crotonates studied.

**Table 3. Estimated Tropospheric Lifetimes of the Unsaturated Esters Studied in This Work with OH Radicals and Cl Atoms**

crotonate	$\tau_{\text{OH}}$ (h)	$\tau_{\text{Cl}}$ (days)	$\tau_{\text{O}_3}$ (days)	$\tau_{\text{NO}_3}$ (days)
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_3$	3 <sup>a</sup>	5 <sup>a</sup>	4 <sup>b</sup>	13 <sup>c</sup>
$\text{CH}_3\text{CH}=\text{CHC}(\text{O})\text{OCH}_2\text{CH}_3$	3 <sup>a</sup>	5 <sup>a</sup>		

<sup>a</sup>Rate coefficients used in the calculation of the lifetimes were taken from this work. <sup>b</sup>Rate coefficients used in the calculation of the lifetimes were taken from ref 30. <sup>c</sup>Rate coefficients used in the calculation of the lifetimes were taken from ref 31.

The lifetimes indicate that the crotonates are likely to be removed rapidly in the gas phase, being the reaction with OH the major loss process for methyl crotonate and ethyl crotonate (around 3 h).

For Cl atom reactions, the tropospheric lifetimes estimated were 5 days for both crotonates. Nevertheless, in marine coastal areas and in inland areas near pollutant sources, where peak concentrations of Cl atoms as high as  $1 \times 10^5$  atom/ $\text{cm}^3$  can occur,<sup>32–34</sup> Cl-atom initiated degradation of methyl and ethyl crotonate can then be a significant homogeneous loss process.

Unfortunately, no data are available of the reactions of  $\text{NO}_3$  radicals and  $\text{O}_3$  molecules with ethyl crotonate. However, on the basis of structural similarities, it is probable that they will show a reactivity toward  $\text{NO}_3$  and  $\text{O}_3$  similar to that of methyl crotonate and thus have a lifetime similar to that of the reaction with the oxidant (on the order of days). Photolytic loss process of the unsaturated esters will be negligible because they are photolytically stable in the actinic region of the electromagnetic spectrum.

Therefore, reactions with OH radicals are likely to dominate the atmospheric removal of methyl crotonate and ethyl crotonate.

The short lifetimes for the esters imply that these compounds will be removed rapidly in the gas phase with a local impact and a possible contribution to the ozone formation in the troposphere.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Mellouki, A.; Le Bras, G.; Sidebottom, H. *Chem. Rev.* **2003**, *103* (12), 5077–5096.
- (2) Pfrang, C.; King, M. D.; Canosa-Mas, C. E.; Flugge, M.; Wayne, R. P. *Atmos. Environ.* **2007**, *41*, 1792–1802.
- (3) Teruel, M. A.; Achad, M.; Blanco, M. B. *Chem. Phys. Lett.* **2009**, *479*, 25–29.
- (4) Graedel, T. E. *Chemical compounds in the atmosphere*; Academic Press: Orlando, FL, 1978.
- (5) Srivastava, S. *Des. Monomers Polym.* **2009**, *12*, 1–18.
- (6) Ryou, M.; Thompson, C. C. *Tech. Gastrointest. Endosc.* **2006**, *8*, 33–37.
- (7) www.basf.com.
- (8) Jacobson, M. C.; Hansson, H. C.; Noone, K. J.; Charlson, R. J. *Rev. Geophys.* **2000**, *38*, 267–294.
- (9) Blanco, M. B.; Barnes, I.; Teruel, M. A. *Chem. Phys. Lett.* **2010**, *488*, 135–139.
- (10) Mellouki, A.; Teton, S.; LeBras, G. *Int. J. Chem. Kinet.* **1995**, *27*, 791–805.
- (11) Albaladejo, J.; Ballesteros, B.; Jimenez, E.; Diaz de Mera, Y.; Martinez, E. *Atmos. Environ.* **2003**, *37*, 2919–2926.
- (12) Teruel, M. A.; Blanco, M. B.; Luque, G. R. *Atmos. Environ.* **2007**, *41*, 5769–5777.
- (13) Saunders, S. M.; Baulch, D. L.; Cooke, K. M.; Pilling, M. J.; Smurthwaite, P. I. *Int. J. Chem. Kinet.* **1994**, *26*, 113–130.
- (14) Teruel, M. A.; Lane, S. I.; Mellouki, A.; Solignac, G.; Le Bras, G. *Atmos. Environ.* **2006**, *40*, 3764–3772.
- (15) Blanco, M. B.; Taccone, R. A.; Lane, S. I.; Teruel, M. A. *Chem. Phys. Lett.* **2006**, *429*, 389–394.
- (16) Blanco, M. B.; Teruel, M. A. *J. Org. Chem.* **2008**, *21*, 397–401.
- (17) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. *J. Phys. Chem. A* **2009**, *113*, 5958–5965.
- (18) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. *Atmos. Environ.* **2009**, *43*, 5996–6002.
- (19) Martín Porrero, M. P.; Gallego-Iniesta García, M. P.; Espinosa Ruiz, J. L.; Tapia Valle, A.; Cabañas Galán, B.; Salgado Muñoz, M. S. *Environ. Sci. Pollut. Res.* **2010**, *17*, 539–546.
- (20) Picquet-Varrault, B.; Doussin, J. F.; Durand-Jolibois, R.; Pirali, O.; Carlier, P. *Environ. Sci. Technol.* **2002**, *36*, 4081–4086.
- (21) Picquet-Varrault, B.; Scarfogliero, M.; Doussin, J. F. *Environ. Sci. Technol.* **2010**, *44*, 4615–4621.
- (22) Blanco, M. B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M. A. *Environ. Sci. Technol.* **2010**, *44*, 7031–7036.
- (23) Smith, M. B.; March, J. *Advances in Organic Chemistry*, 5th ed.; John Wiley & Sons: New York, 2001.
- (24) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215–290.
- (25) Atkinson, R. *Atmos. Environ.* **2000**, *34*, 2063–2101.
- (26) Hein, R.; Crutzen, P. J.; Heimann, M. *Global Biogeochem. Cycles* **1997**, *11*, 43–76.
- (27) Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, T. W.; Blake, D. R.; Rowland, F. S. *J. Geophys. Res.* **1996**, *101*, 4331–4340.
- (28) Shu, Y.; Atkinson, R. *J. Geophys. Res.* **1995**, *100*, 7275–7282.
- (29) Logan, J. A. *J. Geophys. Res.* **1985**, *90*, 463–482.
- (30) Grosjean, D.; Grosjean, E.; Williams, E. L. II. *Int. J. Chem. Kinet.* **1993**, *25*, 783–794.
- (31) Canosa-Mas, C. E.; Flugge, M. L.; King, M. D.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **2005**, *7*, 643–650.
- (32) Ezell, M. J.; Wang, W.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. *J. Phys. Chem. Chem. Phys.* **2002**, *4*, 5813–5820.
- (33) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastidge, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353–356.
- (34) Thornton, J. A.; Kercher, J. P.; Riedel, T. P.; Wagner, N. L.; Cozic, J.; Holloway, J. S.; Dubé, W. P.; Wolfe, G. M.; Quinn, P. K.; Middlebrook, A. M.; et al. *Nature* **2010**, *464*, 271–274.