Rate Constants for $RO_2 + HO_2$ Reactions Measured under a Large Excess of HO_2

Andrew A. Boyd, Pierre-Marie Flaud, Nicolas Daugey, and Robert Lesclaux*

Laboratoire de Physico-Chimie Moléculaire − UMR 5803 CNRS Université Bordeaux I − 33405 Talence Cedex, France

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Rate constants for reactions of various peroxy radicals RO_2 with HO_2 have been measured at room temperature, using laser-flash photolysis and UV absorption spectrometry. The unique feature of those measurements is that they were performed under a large excess of HO_2, so that the only significant reactions were those of HO_2 with itself and with RO_2. It results that the reaction mechanism was considerably simplified, because those reactions are terminating and the generally complex reaction sequence initiated by the RO_2 self-reaction was of negligible importance. In addition, it was not necessary to know the RO_2 concentration accurately, only the HO_2 concentration. The measured rate constants agree with the literature values, when available. The results confirm the increase of rate constants with the size of RO_2 radicals, from nearly 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for CH_3O_2, up to a limit of about 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for $C_{10}-C_{14}$ radicals. Interestingly, RO_2 radicals originating from reactions of OH with terpenes react with rate constants close or equal to this upper limit.

Introduction

Peroxy radicals are key intermediates in oxidation processes of hydrocarbons. They generally exhibit low reactivity toward closed shell molecular species and, consequently, they essentially react with themselves and with other radical species. The reactions of peroxy radicals RO_2 with HO_2,

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (1a)$$

$$\rightarrow \text{other products} \qquad (1b)$$

are among the most important combination reactions of peroxy radicals, either in the atmospheric oxidation of hydrocarbons or in combustion. This importance essentially results from the abundance of the HO_2 radical, which can be formed from various sources in hydrocarbon oxidation processes. In addition, these reactions are generally fast and, thus, contribute significantly to the chemistry of peroxy radicals.[1−4] The only product of reaction 1 that has been clearly characterized is the hydroperoxide ROOH. Another reaction channel, forming ozone, has been shown to occur in the case of acylperoxy radicals $RC(O)O_2$, but this class of radicals is not considered in the present work, for the reasons explained below.

The role of $RO_2 + HO_2$ reactions in the atmosphere is quite important. The reaction is chain terminating because the principal product, ROOH, is stable under atmospheric conditions. Therefore, it constitutes an efficient reservoir that can eventually be photodissociated into RO + OH,[5] thus regenerating radical species. As a consequence, the kinetics and mechanism of $RO_2 + HO_2$ reactions must be known accurately to model the oxidation processes of hydrocarbons under atmospheric conditions.

The kinetics of recombination cross-reactions between radicals are generally difficult to investigate.[1−4] The main reason is that at least three reactions are in competition: the self-reactions of both radicals and the cross-reaction. In addition, in the case of peroxy radicals, RO_2 self-reactions generally initiate complex reaction mechanisms, because new peroxy radicals are often generated in subsequent reactions. Another difficulty may arise from the overlap of UV spectra, as RO_2 reaction kinetics are generally investigated by flash or laser flash photolysis combined with UV absorption spectrometry, where absorption signals result from the contribution of all species, including reactants and products.

In the present work, the rate constants of $RO_2 + HO_2$ reactions were measured using laser flash photolysis, under conditions such that HO_2 was in a large excess compared to the RO_2 radical. This was possible because HO_2 and RO_2 spectra do not totally overlap and our experimental setup allowed us to measure the small signals corresponding to RO_2 radicals at low concentrations. This presents two significant advantages:

(i) Such conditions are similar to pseudo-first-order conditions in which the RO_2 concentration does not need to be known accurately (nor the RO_2 absorption spectrum); only the HO_2 concentration must be well characterized. The RO_2 absorption cross-sections at 210 and 270 nm, where radicals are monitored, must be known for taking its contribution into account in the HO_2 concentration determination, but only approximately because the contribution is small (about 10% of total absorption at 210 nm).

(ii) The reaction mechanism is extremely simplified because RO_2 radicals only react with HO_2 to form unreactive molecular products, essentially the hydroperoxide ROOH. As a result, secondary reactions resulting from RO_2 self-reactions and possible absorption from products are of negligible importance.

The results are presented for a series of RO_2 radicals, including the simplest CH_3O_2 and the more complex ones resulting from the reaction of OH with terpenes. They are compared to the literature data, when available.

Experimental Section

Rate constants were measured using laser-flash photolysis, combined with UV absorption detection of peroxy radicals. The

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* Corresponding author. E-mail: lesclaux@cribx1.u-bordeaux.fr.

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detailed description of the technique has already been reported[6] and only the main features are summarized here. OH radicals were formed by photolysis of H_2O_2 at 248 nm, using an excimer laser (Lambda Physik EMG 200). RO_2 and HO_2 radicals were formed according to the following sequence of reactions:

$$H_2O_2 + h\nu\ (248\ \text{nm}) \rightarrow 2OH \qquad (2)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (3)$$

$$OH + \text{saturated hydrocarbon}\ (+O_2) \rightarrow RO_2 + H_2O \qquad (4)$$

or

$$OH + \text{unsaturated hydrocarbon}\ (+M + O_2) \rightarrow RO_2 \qquad (5)$$

Reaction 5 is an association reaction yielding a hydroxy substituted peroxy radical. In the case of precursors having several possible sites for OH attack, different RO_2 isomers can be formed simultaneously. The results show, however, that this not a real problem, as discussed below.

The reaction cell was a Pyrex tube, either 70 or 100 cm long, 1.8 cm i.d., equipped with quartz windows. The gas mixture, composed of air, H_2O_2, and the hydrocarbon used as the RO_2 precursor, was flowed continuously through the cell, so that it was renewed between two laser pulses. All experiments were performed in air at room temperature and at 1 atm total pressure.

The concentration of peroxy radicals was measured by UV absorption spectrometry, HO_2 at 210 nm (or 220 nm when the RO_2 precursor absorbs at 210 nm, i.e. 1,2-dichloroethene and α-pinene), using its well characterized absorption cross-section,[7] and all RO_2 radicals at 270 nm, where the HO_2 absorption is negligible. No measurements could be performed between 230 and 265 nm, corresponding to the total reflecting spectral range of the dichroic mirrors used to reflect the laser beam into the reaction cell. Time-resolved signals were recorded using a digital oscilloscope and stored in a personal computer for averaging (30−250 traces were averaged) and analysis. Later experiments were performed using a fast analogue to digital converter (400 kHz, 16 bits) instead of the oscilloscope. This provided the interesting possibility of recording signals over a long time scale, for an accurate measurement of any residual absorption, while a high temporal resolution was maintained for kinetic measurements. A typical signal is shown in Figure 1. This procedure was actually used for most experiments, including all compounds. Values of the rate constant k_1 were derived from experimental traces using computer simulation (nonlinear least-squares fitting procedure developed in the laboratory).

Synthetic air ($N_2 + O_2$, 99.995%) was from "AGA gaz speciaux" and H_2O_2 (50% in water) was from Aldrich. The RO_2 precursors, methane (99.995%, "AGA gaz speciaux"), ethane and ethene (99.4%, "AGA gaz speciaux"), neopentane (99% + 0.9% *n*-butane, Merk), cyclohexane (99.9%, Aldrich), decane (>99%, Aldrich), tetradecane (> 99%, Aldrich), cyclohexene (>99%, Aldrich), 1,2-dichloroethene (98%, Aldrich), tetramethylethene (98%, Aldrich), isoprene (>99%, Aldrich), α-pinene (>99%, Aldrich), and *γ*-terpinene and *d*-limonene (97%, Aldrich) were used without further purification. Gas flows were measured using calibrated gas flow controllers, and liquid compounds were injected in the gas stream using temperature controlled bubblers.

Results and Discussion

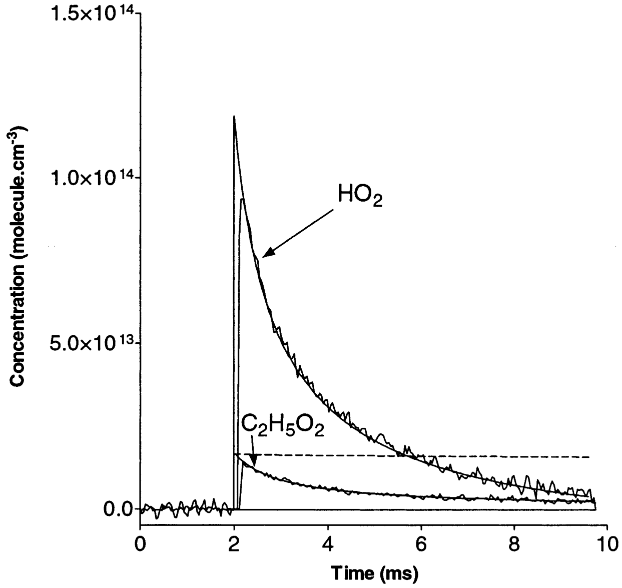

Figure 1. Typical decay traces and their simulations obtained for measurements of $RO_2 + HO_2$ reaction rate constants (particular case of $C_2H_5O_2 + HO_2$). The dashed line represents what would be the $C_2H_5O_2$ decay in the absence of HO_2, showing that $C_2H_5O_2$ reacts almost exclusively with HO_2.

Pairs of decay traces, recorded at 210 and 270 nm, as shown in Figure 1 in the particular case of the $C_2H_5O_2 + HO_2$ reaction, were analyzed by computer simulation, using a simplified reaction mechanism in which the RO_2 radical only reacted with HO_2 and with itself:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (6)$$

$$RO_2 + HO_2 \rightarrow \text{products} \qquad (1)$$

$$RO_2 + RO_2 \rightarrow \text{products} \qquad (7)$$

The use of a simplified mechanism is justified because, due to the large excess of HO_2, only the $HO_2 + HO_2$ and $RO_2 + HO_2$ reactions played a significant role. The role of the RO_2 self-reaction was generally negligible. When the full reaction mechanism was known and thus could be used, no difference was observed in the results. For the highest RO_2 concentrations used, the self-reaction could play a minor role. The rate constant value of the RO_2 self-reaction was either known[1−4] or estimated from the RO_2 decay observed when using a large excess of the RO_2 precursor to form the RO_2 radical alone.

The initial total radical concentration was of the order of 1×10^{14} molecule cm^{-3} when using H_2O_2 concentrations of around 1×10^{16} molecule cm^{-3}. The RO_2 radical concentration was usually between $^1/_4$ and $^1/_{10}$ that of HO_2, as illustrated in Figure 1. This was obtained by adjusting the relative concentrations of H_2O_2 and of the RO_2 precursor. The HO_2 concentration was measured at 210 (or 220) nm, using the recommended absorption cross-section of 4.15×10^{-18} (or 3.41×10^{-18} at 220 nm) cm^2 $molecule^{-1}$.[7] The HO_2 self-reaction rate constant was measured to be in the range $3.5{-}4.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. For a better consistency between experiments, the value was fixed at 3.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. An error of 10% on this value resulted in an error of 2−4% on k_1, in the range of values obtained. To estimate the RO_2 concentration, absorption cross-sections were taken from the literature[1,2,8] or estimated by using a large excess of the RO_2 precursor, by reference to the ethylperoxy radical cross-section.[7]

Rate constants have been measured (or remeasured) for a large variety of RO_2 radicals originating from various hydro-

TABLE 1: Rate Constants for $RO_2 + HO_2$ Reactions at 298 K, 1 atm Air[a]

RO_2 radical	$k_1(298K)^{b,c}$	lit. value[b]	ref
Radicals Obtained by Hydrogen Abstraction			
CH_3O_2	5.13 ± 0.55	5.2	7
$C_2H_5O_2$	8.14 ± 0.38	7.8	7
neo-$C_5H_{11}-O_2$	13.8 ± 2.3	15	17
c-$C_6H_{11}-O_2$	17.1 ± 1.7	17	18
$C_{10}H_{21}-O_2$[d]	19.5 ± 2.1		
$C_{14}H_{29}-O_2$[d]	21.1 ± 2.3		
Radicals Obtained by OH Addition to Unsaturated Compounds			
$HO-(C_2H_4)-O_2$	11.7 ± 2.2	13	3
$HO-(1,2\text{-}C_2H_2Cl_2)-O_2$	5.75 ± 1.2		
HO−(TME)−O_2[e]	15.0 ± 1.5	≈20	19
HO−(isoprene)−O_2	17.4 ± 2.5		
HO−(cyclohexene)−O_2	22.4 ± 2.0		
HO−(α-pinene)−O_2	20.9 ± 1.5		
HO−(γ-terpinene)−O_2	19.7 ± 4.0		
HO−(*d*-limonene)−O_2	21.2 ± 2.9		

[a] Detailed results for each compounds are provided as Supporting Information. Note that the RO_2 radicals originating from terpenes may be partly formed by hydrogen abstraction. [b] Units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. [c] Errors are 2σ. [d] From OH reaction with *n*-decane and *n*-tetradecane. [e] TME for tetramethylethene.

carbons (from methane to terpenes and tetradecane). It must be emphasized that this way of measuring rate constants for $RO_2 + HO_2$ reactions is very simple, reproducible, and quickly done. It must be noted, however, that we have encountered a difficulty with the determination of the HO_2 concentration during the first experiments. According to the rate constant values found for the $HO_2 + HO_2$ reaction and for those $RO_2 + HO_2$ reactions that were already investigated, it appeared that the measured HO_2 concentration was systematically underestimated by about 30%, resulting in rate constants overestimated by the same amount. For example, the rate constant $k(HO_2+HO_2)$ was found to be around 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, whereas a value of about 4×10^{-12} cm^3 $molecule^{-1}$ s^{-1} was expected at 1 atm pressure and in the presence of about 2×10^{17} molecule cm^{-3} of water (actually $H_2O_2 + H_2O$). Similarly, the rate constant for the $HOC_2H_4O_2$ self-reaction was measured to be 30% larger than the recommended value.[3] This deviation was attributed to microgradients of radical concentrations created by some lack of homogeneity of the laser beam. This interpretation was supported by the fact that measurements of rate constants over long time scales (>100 ms), where molecular diffusion tends to homogenize concentrations, yielded the correct values. This was the case, in particular, when measuring the rate constant of the slow $C_2H_5O_2$ self-reaction (7.7×10^{-14} cm^3 $molecule^{-1}$ s^{-1}).[7]

Later, the excimer laser was refurbished and measurements yielded again correct values for test reactions. All experiments already done were then repeated and rate constant values were found in good agreement with those from the first series of measurements, decreased by 30%.

The results are listed in Table 1 and compared to the literature values when available. The quoted uncertainties are the statistical uncertainties (2σ), each value of k_1 resulting from at least five measurements performed with different RO_2 concentrations. Detailed results for each RO_2 radical investigated are provided as Supporting Information: Tables 1S−14S.

The global uncertainties have been estimated to be less than 20% for all reactions. They essentially result from the uncertainty on the determination of the HO_2 concentration (less than 10% as explained below) and from statistical uncertainties (Table 1). Other sources of errors are from the uncertainties on the HO_2 self-reaction rate constant, resulting in 2−4% on k_1, as stated above. Errors on RO_2 absorption cross-sections and self-reaction rate constants are of negligible importance.

The main causes of uncertainties are from HO_2 concentration measurements that are perturbed by the consumption and re-formation of H_2O_2, resulting in a significant absorption offset at 210 (or 220) nm. The value of the offset was determined by measuring the (negative) redidual absorption at long time scale, thus allowing us to take into account in simulations the H_2O_2 direct photolysis, the $OH + H_2O_2$ reaction, and the H_2O_2 re-formation from the HO_2 self-reaction. In addition, losses of species by the $OH + HO_2$ reaction were also taken into account using this procedure as well as, in a few cases, an additional offset due to the precursor absorption bleaching (for terpenes in particular). Errors of about 10% on the HO_2 concentration could result from this procedure. When the absorption of the RO_2 precursor was too strong at 210−220 nm (case of isoprene), the HO_2 concentration was measured in the absence of the precursor and then corrected by subtracting the RO_2 concentration. It was verified in the cases of nonabsorbing precursors that this procedure did not introduce significant additional errors. This was expected because the extent of the correction never exceeded 10−15%.

The direct photolysis of the RO_2 precursor at 248 nm by the laser beam, which might have introduced undesirable radical species in the reacting system, was also considered as a possible source of errors. Apparently, this was not the case, considering the independence of the measured k_1 values with the precursor concentration. In addition, no transient absorption could be detected in the absence of H_2O_2. The reason for this absence of observable precursor photolysis is the very low concentrations used, particularly for the compounds that are likely to absorb at 248 nm (terpenes), because their reactions with OH are generally very fast ($k \approx 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}).

Unfortunately, the method developed in this work for measuring the $RO_2 + HO_2$ reaction rate constants cannot be applied to the acylperoxy $RC(O)O_2 + HO_2$ reactions. The reason is that those reactions produce ozone with yields of about 20% (measured in the case of the $CH_3C(O)O_2$ radical)[9] and the buildup of the ozone absorption compensates almost exactly the $RC(O)O_2$ absorption decay in the 250−280 nm spectral range. Thus, no information can be drawn from the resulting almost flat trace. However, the reactivity of this class of radicals is assumed to be quasi independent of the nature and structure of the R group and to be essentially controlled by the $-C(O)O_2$ group.[10,11] This is the case, for example, for $RC(O)O_2$ self-reactions.[11] Consequently, it is presently admitted that all rate constants of $RC(O)O_2 + HO_2$ reactions are likely to be close to the value of 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} determined for the $CH_3C(O)O_2$.[9] However, recent results in our laboratory, which have to be confirmed, indicate that this may not be the case for larger radicals ($(CH_3)_3CC(O)O_2$, for example), which seem to react significantly faster with HO_2.

It is seen that the k_1 values measured in this work agree with literature values, when available, within uncertainties. New rate constants are reported in this work for $RO_2 + HO_2$ reactions that have not been investigated before, in particular for the RO_2 radicals formed in the reaction of OH with terpenes. A relationship between structure and reactivity was previously proposed by Jenkin,[12] indicating that rate constants of $RO_2 + HO_2$ reactions increase with the number of carbon atoms of the RO_2 radical, from 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for CH_3O_2 to an upper limit of about 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the largest radicals investigated. Obviously this trend is confirmed by the present measurements, as seen in Figure 2. The

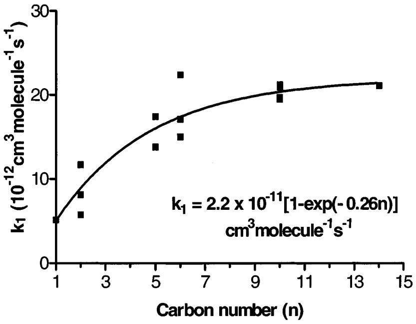

Figure 2. Dependence of the $RO_2 + HO_2$ reaction rate constants with the number of carbon atoms in RO_2 radicals.

corresponding relationship, $k_1/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} = 2.2 \times 10^{-11}$ $[1 - \exp(-0.26n)]$ (n being the number of carbon atoms), is very close to the expression previously proposed by Jenkin.[12] Other data reported in the literature for the $(CH_3)_2C(OH)CH_2O_2 + HO_2$[13] and $c\text{-}C_5H_9O_2 + HO_2$[14] reactions ($k/10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} = 1.4 and 1.5, respectively) are in very good agreement with the above relationship. Some deviations are observed from rate constants predicted by this relationship, but they are hardly over experimental uncertainties. However, this probably means that the relationship is too simple and that other parameters should be taken into account. In particular, it seems that hydroxy-substituted peroxy radicals, formed from OH addition to unsaturated precursors, exhibit slightly larger rate constants than unsubstituted radicals. In contrast, halogenated radicals may tend to react more slowly than the corresponding unsubstituted radicals, as seen in this work for the $HOCHCl-CHClO_2$ radical. This should be confirmed but, nevertheless, the above relationship seems to predict rate constants with an uncertainty that is of the order of magnitude of experimental uncertainties, i.e., about 20%. It also accounts reasonably well for other data from the literature.[3,4] However, it does not hold for perfluorinated radicals that exhibit much slower reactions.[3,4]

The striking feature of the $RO_2 + HO_2$ reaction kinetics is that rate constants only vary by a factor 4−4.5 for radicals having very different structures, whereas RO_2 self-reaction rate constants can vary by several order of magnitude.[1−3] This indicates that the reaction mechanism is very similar for all RO_2 radicals, independently of their structure. It is established that rate constants of $RO_2 + HO_2$ reactions generally exhibit negative temperature dependence, showing the presence of a potential well on the reaction coordinate, with an exit barrier toward products corresponding to the rearrangement of the intermediate species.[1−4] That the rate constant increases with the size of the radical indicates that, for some reason, the decomposition of the intermediate complex (tetroxyde ROOOOH) toward products becomes faster and only sophisticated quantum calculations could explain this behavior. However, calculations involving this type of tetroxide have been proved to be difficult and poorly reliable. The observed upper limit may simply correspond to the rate constant of the association reaction (entrance channel). This increase of rate constants with the size of the radical has also been observed for self-reactions of different RO_2 radicals, such as alkylperoxy radicals,[1−3,15] or β-hydroxyperoxy radicals,[16] with an upper limit as observed in the present case. Thus, this behavior seems to be general for self- and cross-reactions of peroxy radical.

It should be emphasized that, for some of the radicals investigated in this work, several RO_2 isomers could be formed by OH attack on different sites of the precursor molecule. Nevertheless, the results remain significant because the principal parameter that determines the rate constant is the size rather than the structure of the radical. In addition, this mainly occurs in the cases of largest radicals, for which rate constant values are close to the upper limit and, thus, do not vary significantly from one radical to the other or from one isomer to the other.

The interesting point in the present measurements is that all reactions of RO_2 radicals originating from OH reactions with terpenes exhibit rate constant values close to the upper limit of 2.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Thus the high efficiency of those reactions shows that formation of hydroperoxides must be an efficient process in the case of terpene oxidation in the atmosphere, under low NO_x conditions.

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Supporting Information Available: Detailed results for the 14 compounds investigated in this work are provided in Tables 1S to 14S. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmos. Environ. Part A* **1992**, *26A*, 1805−1961.

(2) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev.* **1992**, *92*, 667−710.

(3) Lesclaux, R. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1997; Chapter 6, pp 81−112.

(4) Wallington, T. J.; Nielsen, O. J.; Sehested, J. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1997; Chapter 7, pp 113−172.

(5) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *NASA JPL Pub.* **1997**, 97−4.

(6) Fenter, F. F.; Lightfoot, P. D.; Niiranen, J. T.; Gutman, D. *J. Phys. Chem.* **1993**, *97*, 5313−5320.

(7) Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Pilling, M. J.; Ravishankara, A. R.; Wallington, T. J. *J. Geophys. Res.* **2001**, *106*, 12157−12183.

(8) Nielsen, O. J.; Wallington, T. J. In *Peroxyl Radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1997; Chapter 5, pp 69−80.

(9) Tomas, A.; Villenave, E.; Lesclaux, R. *J. Phys. Chem. A* **2001**, *105*, 3505−3514.

(10) Villenave, E.; Lesclaux, R.; Seefeld, S.; Stockwell, W. R. *J. Geophys. Res.* **1998**, *103*, 25273−25285.

(11) Tomas, A.; Lesclaux, R. *Chem. Phys. Lett.* **2000**, *319*, 521−528.

(12) Jenkin, M. E. "SARBVOC" final report, Contract No ENV4-CT95-0031, Commission of the European Union, 1998.

(13) Boyd, A. A.; Lesclaux, R.; Jenkin, M. E.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 6594−6603.

(14) Crawford, M. A.; Szente, J. J.; Maricq, M. M.; Francisco, J. S. *J. Phys. Chem. A* **1997**, *101*, 5337−5343.

(15) Boyd, A. A.; Villenave, E.; Lesclaux, R. *Int. J. Chem. Kinet.* **1999**, *31*, 37−46.

(16) Boyd, A. A.; Villenave, E.; Lesclaux R. To be submitted.

(17) Rowley, D. M.; Lesclaux, R.; Lightfoot, P. D.; Hughes, K.; Hurley, M. D.; Rudy, S. *J. Phys. Chem.* **1992**, *96*, 7043−7048.

(18) Rowley, D. M.; Lesclaux, R.; Lightfoot, P. D.; Noziere, B.; Wallington, T. J.; Hurley, M. D. *J. Phys. Chem.* **1992**, *96*, 4889−4894.

(19) Jenkin, M. E.; Hayman, G. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1911−1922.