Kinetics of the Cross Reactions of CH_3O_2 and $C_2H_5O_2$ Radicals with Selected Peroxy Radicals

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The kinetics of the reactions of selected peroxy radicals (RO_2) with CH_3O_2 and with $C_2H_5O_2$ have been investigated using two techniques: excimer-laser photolysis and conventional flash photolysis, both coupled with UV absorption spectrometry. Radicals were generated either by photolysis of molecular chlorine in the presence of suitable hydrocarbons or by photolysis of the appropriate alkyl chloride. All such cross-reaction kinetics were investigated at 760 Torr total pressure and room temperature except for the reaction of the allylperoxy radical with CH_3O_2, for which the rate constant was determined between 291 and 423 K, resulting in the following rate expression: $k_{15} = (2.8 \pm 0.7) \times 10^{-13} \exp[(515 \pm 75)/T]$ cm^3 molecule^{-1} s^{-1}. Values of $(2.0 \pm 0.5) \times 10^{-13}$, $(1.5 \pm 0.5) \times 10^{-12}$, $(9.0 \pm 0.15) \times 10^{-14}$, $<2.0 \times 10^{-12}$, $(2.5 \pm 0.5) \times 10^{-12}$, and $(8.2 \pm 0.6) \times 10^{-12}$ (units of cm^3 molecule^{-1} s^{-1}) have been obtained for the reactions of CH_3O_2 radicals with $C_2H_5O_2$, *neo*-$C_5H_{11}O_2$, *c*-$C_6H_{11}O_2$, $C_6H_5CH_2O_2$, CH_2ClO_2, and $CH_3C(O)O_2$, respectively, and $(1.0 \pm 0.3) \times 10^{-12}$, $(5.6 \pm 0.8) \times 10^{-13}$, $(4.0 \pm 0.2) \times 10^{-14}$, and $(1.0 \pm 0.3) \times 10^{-11}$ (units of cm^3 molecule^{-1} s^{-1}) for the reactions of $C_2H_5O_2$ with $CH_2{=}CHCH_2O_2$, *neo*-$C_5H_{11}O_2$, *c*-$C_6H_{11}O_2$, and $CH_3C(O)O_2$ radicals, respectively. These rate constants were obtained by numerical simulations of the complete reaction mechanisms, which were deduced from the known mechanisms of the corresponding peroxy radical self-reactions. A systematic analysis of propagation of errors was carried out for each reaction to quantify the sensitivity of the cross-reaction rate constant to the parameters used in kinetic simulations. The rate constant for a given cross reaction is generally found to be between the rate constants for the self-reactions of RO_2 and CH_3O_2 (or $C_2H_5O_2$). However, when the RO_2 self-reaction is fast, the cross reaction with CH_3O_2 (or $C_2H_5O_2$) is also fast, with similar rate constants for both reactions, suggesting that these particular peroxy radical cross reactions can play a significant role in the chemistry of hydrocarbon oxidation processes in the troposphere and in low-temperature combustion. Relationships between cross-reaction and self-reaction rate constants are suggested.

Introduction

The kinetics and mechanisms of peroxy radical (RO_2) reactions have received a great deal of attention during recent years as a result of their importance in the oxidation process of hydrocarbons and halocarbons.[1,2] Owing to the very large number of peroxy radicals that can be formed, either in tropospheric chemistry or in low-temperature combustion, modeling of hydrocarbon oxidation processes requires kinetic and mechanistic data to be determined for model radicals, with the objective of establishing relationships between structure and reactivity.

The tropospheric chemistry of peroxy radicals involves several competing reactions, depending on the distribution of relevant trace atmospheric constituents. Under high NO_x concentrations, RO_2 radicals react principally with NO and NO_2:

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (1a)$$

$$\xrightarrow{\text{M}} RONO_2 \qquad (1b)$$

$$RO_2 + NO_2 + M \leftrightharpoons RO_2NO_2 + M \qquad (2)$$

On the other hand, it is widely accepted that the principal loss process for peroxy radicals in the troposphere under low NO_x concentrations is by reaction with HO_2:

$$RO_2 + HO_2 \rightarrow ROOH \text{ (or other products)} \qquad (3)$$
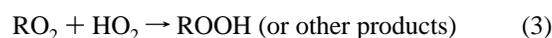
However, in hydrocarbon-rich remote atmospheres (marine boundary layer, forest areas) or in low-temperature combustion, it has been shown that high concentrations of RO_2 radicals can build up so that RO_2 self-reactions and cross reactions must be taken into account.[3,4]

$$RO_2 + RO_2 \rightarrow \text{products} \qquad (4)$$

$$RO_2 + R'O_2 \rightarrow \text{products} \qquad (5)$$
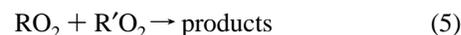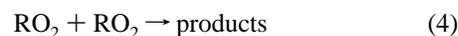
According to the established degradation processes of hydrocarbons, which involve successive C−C bond splitting, the smallest radicals reach the highest concentrations. As a result, CH_3O_2, $C_2H_5O_2$, and $CH_3C(O)O_2$ are the most abundant radicals along with HO_2. In particular, the CH_3O_2 radical may reach concentrations as high as those of HO_2, *i.e.*, around 10^8-10^9 molecule cm^{-3} in the troposphere.[3] $C_2H_5O_2$ and $CH_3C(O)O_2$ may also reach fairly high concentrations, though a factor of 5−10 lower. Therefore, it is expected that cross reactions of RO_2 radicals with these most abundant radicals play a significant role in hydrocarbon oxidation processes, provided they are fast enough. A knowledge of the rate constants of such cross reactions is therefore of great interest.

At the present time, very few cross reactions of peroxy radicals have been studied.[1,2] As far as $RO_2 + CH_3O_2$ reactions are concerned, only a few rate constants have been estimated

as part of the studies of some RO$_2$ self-reactions in which the CH$_3$O$_2$ radical is produced by secondary chemistry. This was the case for the reactions of CH$_3$C(O)O$_2$,[5] CH$_3$C(O)CH$_2$O$_2$,[6] and t-C$_4$H$_9$O$_2$[7,8] radicals. More recently, a kinetic study of the cross reaction CCl$_3$O$_2$ + CH$_3$O$_2$ has been carried out in our laboratory[9] as part of a study of chloromethylperoxy radical reactions. No other studies of cross reactions involving C$_2$H$_5$O$_2$ or CH$_3$C(O)O$_2$ have been reported so far.

We have investigated in the present work the kinetics of a series of peroxy radical cross reactions with CH$_3$O$_2$ for various typical RO$_2$ radicals: CH$_2$=CHCH$_2$O$_2$, C$_2$H$_5$O$_2$, neo-C$_5$H$_{11}$O$_2$, c-C$_6$H$_{11}$O$_2$, C$_6$H$_5$CH$_2$O$_2$, CH$_2$ClO$_2$, and CH$_3$C(O)O$_2$. The cross reactions of C$_2$H$_5$O$_2$ with a few of these radicals have also been investigated. These radicals have been chosen, since they represent typical classes of peroxy radicals, with the aim of establishing structure−reactivity relationships. In addition, the mechanism and rate constants of the self-reactions, which must be known in cross reaction studies, have been already determined for all these radicals.[1,2,10−12] The investigation of cross reactions involving the acetylperoxy radical is in progress and will be reported separately.
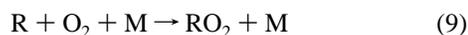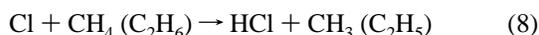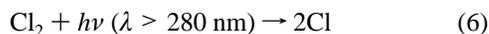
Experiments were performed using two techniques: pulsed excimer-laser photolysis and conventional argon-lamp flash photolysis, both using UV absorption spectrometry for real-time monitoring of radical concentrations. In the case of the reaction of the allylperoxy radical with CH$_3$O$_2$, the temperature dependence of the rate constant was measured from 291 to 423 K and compared to temperature dependences of other primary peroxy radical self-reactions.[1,2] All other experiments were carried out at room temperature and atmospheric pressure.

Experimental Section

Both experimental techniques employed in this study have been already described in the literature,[13,14,10] and only the main features are given below.

Flash Photolysis/UV Absorption Apparatus. The apparatus consisted of a 70 cm long cylindrical Pyrex cell through which the gas mixture was in continuous flow. Flashes were generated by discharging two capacitors through external argon flash lamps. Radical concentrations were monitored using time-resolved UV absorption spectrometry at various wavelengths between 200 and 300 nm. The analysis beam from a deuterium lamp passed twice through the cell and was focused onto the slit of a monochromator−photomultiplier unit. The signal was stored in a digital oscilloscope and transferred to a microcomputer for signal averaging and further data analysis.
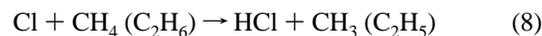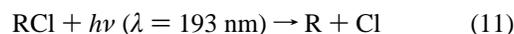
Peroxy radicals RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) were generated using the near-UV photolysis of Cl$_2$, at wavelengths longer than the Pyrex cutoff, in the presence of gas mixtures containing the appropriate concentrations of the corresponding precursor RH, methane (or ethane), and oxygen according to the following reaction sequence:

$$Cl_2 + h\nu \ (\lambda > 280 \text{ nm}) \rightarrow 2Cl \qquad (6)$$

$$Cl + RH \rightarrow HCl + R \qquad (7)$$

$$Cl + CH_4 \ (C_2H_6) \rightarrow HCl + CH_3 \ (C_2H_5) \qquad (8)$$

$$R + O_2 + M \rightarrow RO_2 + M \qquad (9)$$

$$CH_3 \ (C_2H_5) + O_2 + M \rightarrow CH_3O_2 \ (C_2H_5O_2) + M \ \ (10)$$

followed by the corresponding self-reactions, cross reactions, and subsequent secondary reactions of peroxy and alkoxy radicals.

This method was used in the particular cases of benzylperoxy, cyclohexylperoxy, and acetylperoxy radicals. The concentration of molecular chlorine was measured by its absorption at 330 nm ($\sigma = 2.56 \times 10^{-19}$ cm^2 molecule^{-1})[15] and maintained in the range 1.5×10^{16} to 4.5×10^{16} molecule cm^{-3}. The concentrations of the precursor RH, methane (or ethane), and oxygen were chosen such that the conversion of chlorine atoms into radicals was very rapid (<5 μs) compared to the time scale of the reactions of interest (>20 ms) and dominated all other loss processes of Cl atoms. In addition, relative concentrations of RH and CH$_4$ (or C$_2$H$_6$) were such that comparable concentrations of RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) were generated simultaneously. The total concentration of radicals was determined by producing CH$_3$O$_2$ alone using its well-known UV absorption cross sections.[1,2] The relative concentrations of RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) were determined from the relative concentrations of precursors and from the rate constants of their reactions with chlorine atoms. However, in the case of the acetylperoxy radical, relative concentrations could be determined by monitoring its typical absorption at 207 nm, while that of the methyl- (or ethyl-) peroxy radical was monitored at 240 nm. The gas mixtures were prepared by diluting Cl$_2$, RH, methane (or ethane), and oxygen into a large flow of nitrogen using calibrated flow controllers at a total pressure of 760 Torr. Under these experimental conditions, initial radical concentrations were in the range 1.5×10^{13} to 7.0×10^{13} molecule cm^{-3}. The total flow rate was sufficiently high to ensure that the reaction mixture in the cell was completely replenished between each flash, thus preventing complications arising from reaction products.

Laser-Flash Photolysis/UV Absorption Apparatus. The apparatus consisted of a cylindrical Pyrex reaction cell (80 cm in length) bearing a Suprasil-grade quartz window at each end. The cell could be heated to about 500 K.[10] The beam of an excimer laser (Lambda Physik Model EMG 200) was directed lengthwise through the cell to photolyze the radical precursors. RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) were generated by photolysis at 193 nm of the corresponding alkyl chloride, either RCl or CH$_3$-Cl, in the presence of CH$_4$ (or C$_2$H$_6$) or RH, respectively:

$$RCl + h\nu \ (\lambda = 193 \text{ nm}) \rightarrow R + Cl \qquad (11)$$

$$Cl + CH_4 \ (C_2H_6) \rightarrow HCl + CH_3 \ (C_2H_5) \qquad (8)$$

followed by reactions 9 and 10. This method was used for the studies of the reactions of CH$_2$=CHCH$_2$O$_2$ and CH$_2$ClO$_2$ with CH$_3$O$_2$ and of CH$_2$=CHCH$_2$O$_2$ with C$_2$H$_5$O$_2$.

However, in studies of C$_2$H$_5$O$_2$ and neo-C$_5$H$_{11}$O$_2$ reactions, the rate of reaction of Cl atoms with the appropriate precursor RCl was too fast and could not be avoided completely, so the photolysis of CH$_3$Cl was preferred to that of RCl.

$$CH_3Cl + h\nu \ (\lambda = 193 \text{ nm}) \rightarrow CH_3 + Cl \qquad (12)$$

$$Cl + RH \rightarrow HCl + R \qquad (7)$$
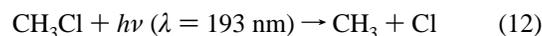
followed by reactions 9 and 10. Note that in both methods, equal concentrations of RO$_2$ and CH$_3$O$_2$ were generated, thus providing the best conditions for investigating the cross-reaction kinetics.

The detection system was the same as described above for the argon-lamp flash photolysis apparatus. Concentrations of precursors were adjusted so that the absorption of the laser beam at 193 nm was always in the range 20−40%. Larger absorptions would have resulted in unsuitable longitudinal radical concentration gradients and associated complications.[10]

Radical concentrations were typically monitored at 235 nm, which corresponds to the maximum of the UV absorption

spectrum of most peroxy radicals. In addition to the radical absorption, two other effects had to be taken into account, which resulted in an additional absorption signal at this wavelength: (*i*) a slight decrease in the transmission of optical elements (dichroic mirrors and windows) when impinged upon by the 193 nm laser pulse, resulting in an almost constant transient absorption of about 0.5−1%; (*ii*) the formation of ozone due to the photolysis of oxygen at 193 nm:

$$O_2 + h\nu \ (193 \text{ nm}) \rightarrow 2O(^3P) \qquad (13)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (14)$$
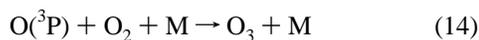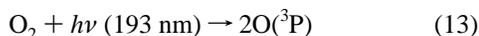
The amount of ozone formed in the system was generally on the order of $(2-5) \times 10^{12}$ molecule cm^{-3}, *i.e.*, an order of magnitude lower than the total initial radical concentration. Such a concentration was too low to perturb significantly the reaction system. Other possible reactions of oxygen atoms leading to the formation of radical species were also negligible under our experimental conditions.

To prevent too high a concentration of ozone being formed and to ensure a stochiometric conversion of radicals (R and CH$_3$ (or C$_2$H$_5$)) into peroxy radicals, the concentrations of oxygen had to be adjusted within a fairly narrow range (typically from 2.5×10^{17} to 7.0×10^{17} molecule cm^{-3}).

The combination of both the above effects resulted in a slightly decreasing transient signal, which generally represented 20−30% of the total initial absorption. It was calibrated before and after each experiment in the absence of any radical precursor and taken into account in simulations as previously described.[10] It was confirmed before each experiment that the conditions were appropriate and the technique viable by photolyzing CH$_3$-Cl in concentrations that gave roughly the same fractional absorption of the laser beam as above (in the presence of methane and oxygen) to generate CH$_3$O$_2$ radicals alone. The rate constant for the CH$_3$O$_2$ self-reaction was then measured and verified to compare favorably with the well-known value reported in the literature.[1,2]

The laser was operated at repetition rates of 0.25−0.40 Hz to ensure that the gas mixture was replenished between each pulse. A typical experiment required between 80 and 160 laser shots to obtain a satisfactory signal-to-noise ratio.

Gas mixtures were introduced via a glass vacuum line using calibrated gas-flow controllers. Liquid radical precursors, such as CH$_2$=CHCH$_2$Cl, *c*-C$_6$H$_{12}$, CH$_2$Cl$_2$, CH$_3$CHO, or C$_6$H$_5$CH$_3$, were introduced into the gas mixture by passing a slow flow of nitrogen through a bubbler containing the appropriate precursor cooled in a water−ice bath.

Oxygen, nitrogen, synthetic air, methane (AGA Gaz spéciaux, >99.995%), ethane (AGA Gaz spéciaux, 99.4%), chlorine (AGA Gaz spéciaux, 5% in nitrogen, >99.9%), chloromethane (L'Air Liquide, >99.5%), chloroethane (Aldrich, 99.7%), dichloromethane (Aldrich, 99.9%), allyl chloride (Aldrich, 99%), acetaldehyde (Aldrich, 99%), toluene (Aldrich, 99.5%), neopentane (ARGO int.Ltd., 99.0%), and cyclohexane (SDS, 99.5%) were all used without further purification. Synthetic air was employed as the main carrier gas in flash photolysis experiments. However, nitrogen was used instead in laser-flash photolysis experiments in which oxygen had to be limited to low concentrations to minimize the previously discussed formation of ozone.

Data Analysis. A typical decay trace is shown in Figure 1 for the case of the reaction of CH$_2$=CHCH$_2$O$_2$ (allylperoxy) with CH$_3$O$_2$. Decay traces were analyzed by numerical integration of a set of differential equations that took into account the
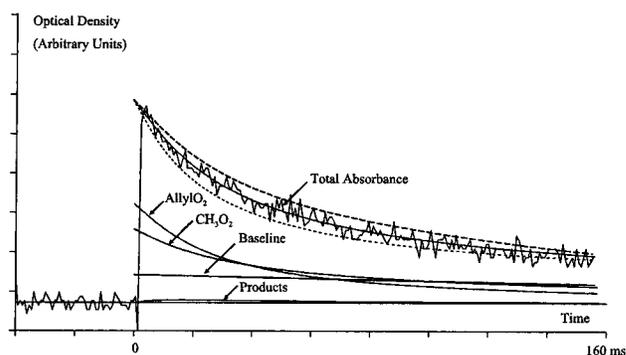

Figure 1. Experimental decay trace recorded at 235 nm and best-fit simulation (solid line) for the cross reaction of CH$_2$=CHCH$_2$O$_2$ with CH$_3$O$_2$ at room temperature. Dashed line represents simulations with k_{15} changed by ±40%.

complete reaction mechanism and simulated by adjusting selected parameters (rate constant and initial concentration) using nonlinear least-squares fitting.

As an example, the reaction mechanism is detailed in the particular case of the CH$_2$=CHCH$_2$O$_2$ + CH$_3$O$_2$ reaction in Table 1. For all the RO$_2$ radicals investigated, the corresponding mechanism included the following reactions: self and cross reactions of RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$), including the terminating and nonterminating channels; the reactions of alkoxy radicals, *i.e.*, reaction with O$_2$ (forming HO$_2$) and/or decomposition; the reactions of RO$_2$ and CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) with HO$_2$, assumed to produce the corresponding hydroperoxides; the reactions of peroxy radicals produced by the decomposition of the alkoxy radicals; the self-reaction of HO$_2$.

In addition to the UV absorption of peroxy radicals and HO$_2$, the absorption of all products (carbonyls, H$_2$O$_2$, and hydroperoxides) was included in simulations of decay traces despite their small contribution (Figure 1). Where UV absorption spectra were unavailable, the spectra of structurally similar compounds were used instead, and the unknown absorption cross sections used in simulations were assumed to be identical with those known for this surrogate.

A particular concern with these experiments was the sensitivity of the system to the various parameters used in simulations. It should be pointed out that the experimental conditions were such that the kinetic simulations were particularly sensitive to the rate constant of the fastest RO$_2$ + RO$_2$ reaction and to that of the RO$_2$ + CH$_3$O$_2$ (or C$_2$H$_5$O$_2$) reaction, provided the latter was not too small (generally not less than a factor of about 5 smaller than the highest RO$_2$ + RO$_2$ reaction rate constant). This was the case for most reactions investigated in this work, except for the benzyl peroxy radical, for which only an upper limit of the cross-reaction rate constant could be determined. The uncertainty of the rate constants of cross reactions is strongly dependent on the parameters used in simulations and on the knowledge of the reaction mechanism. This is the main reason that has led us to study RO$_2$ radicals whose self-reaction had already been investigated in detail.

Results

Studies of the cross reactions of the CH$_2$=CHCH$_2$O$_2$, C$_2$H$_5$O$_2$, *neo*-C$_5$H$_{11}$O$_2$, *c*-C$_6$H$_{11}$O$_2$, C$_6$H$_5$CH$_2$O$_2$, CH$_2$ClO$_2$, and CH$_3$C-(O)O$_2$ radicals with CH$_3$O$_2$ and of the CH$_2$=CHCH$_2$O$_2$, *neo*-C$_5$H$_{11}$O$_2$, *c*-C$_6$H$_{11}$O$_2$, and CH$_3$C(O)O$_2$ radicals with C$_2$H$_5$O$_2$ are reported below. The reaction of the allylperoxy radical CH$_2$=CHCH$_2$O$_2$ with CH$_3$O$_2$ has been selected as a typical case for a detailed presentation of the results and for a study of the temperature dependence of the rate constant. The results for other reactions are only briefly reported, since experiments and
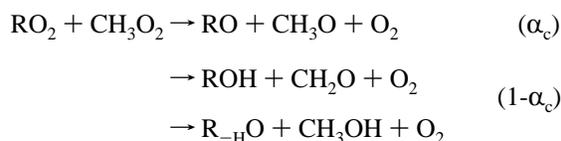
TABLE 1: Reaction Mechanism Used in Simulations of the CH_2=$CHCH_2O_2$ + CH_3O_2 Cross Reaction

reaction	rate constant[a] (298 K)	ref
CH_2=$CHCH_2Cl + h\nu \rightarrow CH_2$=$CHCH_2 + Cl$		
$CH_4 + Cl \rightarrow CH_3 + HCl$	1.0×10^{-13}	16
CH_2=$CHCH_2 + O_2 + M \rightarrow CH_2$=$CHCH_2O_2 + M$	6.0×10^{-13}	17
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	1.21×10^{-12}	16
CH_2=$CHCH_2O_2 + CH_3O_2 \rightarrow CH_2$=$CHCH_2O + CH_3O + O_2$		
CH_2=$CHCH_2O_2 + CH_3O_2 \rightarrow CH_2$=$CHCH_2OH + CH_2O + O_2$	1.7×10^{-12}	this work
CH_2=$CHCH_2O_2 + CH_3O_2 \rightarrow CH_2$=$CHCHO + CH_3OH + O_2$		
CH_2=$CHCH_2O_2 + CH_2$=$CHCH_2O_2 \rightarrow 2CH_2$=$CHCH_2O + O_2$	4.3×10^{-13}	10, 18
CH_2=$CHCH_2O_2 + CH_2$=$CHCH_2O_2 \rightarrow CH_2$=$CHCH_2OH + CH_2$=$CHCHO + O_2$	2.7×10^{-13}	10, 18
$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	1.22×10^{-13}	1, 2
$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$	2.48×10^{-13}	1, 2
$CH_3O + O_2 \rightarrow HO_2 + CH_2O$	2.0×10^{-15}	16
CH_2=$CHCH_2O + O_2 \rightarrow HO_2 + CH_2$=$CHCHO$	$2.0 \times 10^{-15\,b}$	
CH_2=$CHCH_2O_2 + HO_2 \rightarrow CH_2$=$CHCH_2OOH + O_2$	1.0×10^{-11}	10
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	5.8×10^{-12}	1, 2
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.0×10^{-12}	1, 2

[a] Units of cm^3 molecule^{-1} s^{-1}. [b] Assumed equal to methyl analogue.

data analysis were conducted in a similar way. Only the particular features of each of the other cross reactions are emphasized.

For most systems investigated, the reaction mechanism is known, or at least can be reasonably assumed from the known mechanism of the RO_2 and CH_3O_2 (or $C_2H_5O_2$) self-reactions. The main uncertainty is the branching ratio for the terminating and nonterminating channels of the cross reaction $RO_2 + CH_3O_2$ (or $C_2H_5O_2$) (1-α_c and α_c, respectively), which have not been determined. For $RO_2 + CH_3O_2$, the possible reaction channels are

$$RO_2 + CH_3O_2 \rightarrow RO + CH_3O + O_2 \qquad (\alpha_c)$$

$$\rightarrow ROH + CH_2O + O_2 \qquad (1\text{-}\alpha_c)$$

$$\rightarrow R_{-H}O + CH_3OH + O_2$$

where $R_{-H}O$ is a carbonyl compound (aldehyde, ketone, or acid).

Following Madronich *et al.*,[3] we have found it reasonable to assume that, in all systems, α_c can be taken as the arithmetic average of the α values that have been determined for the corresponding self-reactions (where α is the ratio of the rate constant for the alkoxy channel to the total self-reaction rate constant). There is no particular chemical property that can be put forward to justify this assumption, but it should normally minimize the errors due to the use of an erroneous value of α_c. It should also be emphasized that for most systems, the branching ratios for the individual self-reactions are close to each other and, therefore, it is reasonable to assume that the branching ratio for the cross reaction has a similar value. The uncertainty introduced by this assumption is discussed below for each individual system.
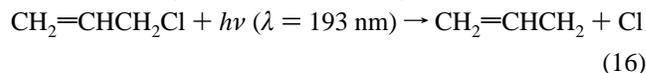
Reactions of the Allylperoxy Radical with CH_3O_2 and $C_2H_5O_2$. The following reaction channels are expected for the reaction with CH_3O_2:

$$CH_2\text{=}CHCH_2O_2 +$$
$$CH_3O_2 \rightarrow CH_2\text{=}CHCH_2O + CH_3O + O_2 \qquad (15a)$$
$$\rightarrow CH_2\text{=}CHCH_2OH + CH_2O + O_2 \qquad (15b)$$
$$\rightarrow CH_2\text{=}CHCHO + CH_3OH + O_2 \qquad (15c)$$

The kinetics of the reaction of the allylperoxy radical with CH_3O_2 were investigated simultaneously as part of a study of the CH_2=$CHCH_2O_2$ radical self-reaction and of its reaction with HO_2.[10] The radicals were generated by laser photolysis of allyl chloride at 193 nm in the presence of excess methane and oxygen. The determination of k_{15} was carried out at six temperatures between 291 and 423 K at 760 Torr and monitored at 235 nm, which corresponds to the maximum of both the allylperoxy and methylperoxy spectra.[1,2,18] The decay time was always 200 ms, which was the most appropriate for kinetic analysis.

The concentration of methane was high enough ($(2.2-3.6) \times 10^{18}$ molecule cm^{-3}) to ensure that all chlorine atoms were stochiometrically converted into methyl radicals:

$$CH_2\text{=}CHCH_2Cl + h\nu \,(\lambda = 193 \text{ nm}) \rightarrow CH_2\text{=}CHCH_2 + Cl \qquad (16)$$

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (8)$$

with $k_8 = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.[16]

The principal possible secondary reaction for chlorine atoms was the reaction with allyl chloride:

$$Cl + CH_2\text{=}CHCH_2Cl \rightarrow \text{products} \qquad (17)$$
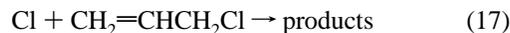
with $k_7 = 1.87 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.[19]

Thus, the loss of chlorine atoms through reaction 17 was never larger than 10%. The allyl chloride concentration was controlled in the cell by its absorption at 193 nm. Cross sections of allyl chloride have been measured using a UV CARY 2000 spectrophotometer, and the value obtained was $\sigma = (5.4 \pm 0.5) \times 10^{-18}$ cm^2 molecule^{-1} at 193 nm. The concentration was maintained in the range 3.2×10^{14} to 10.2×10^{14} molecule cm^{-3} (0.01–0.03 Torr) so that the absorption of the laser beam was limited to less than 30%, thus ensuring relatively small concentration gradients along the cell. The photolysis produced peroxy radical concentrations between 0.9×10^{13} and 7.0×10^{13} molecule cm^{-3} for a laser pulse energy varying between 5 and 30 mJ cm^{-2}.

The stochiometric conversion of radicals into peroxy radicals was ensured by adding an excess of oxygen:

$$CH_2\text{=}CHCH_2 + O_2 + M \rightarrow CH_2\text{=}CHCH_2O_2 + M \qquad (18)$$
$$\text{with } k_{18} = 6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 760 Torr }^{17}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (10)$$
$$\text{with } k_{10} = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 760 Torr }^{15}$$

The low allyl$-O_2$ bond dissociation energy[17] means that there exists the possibility that reaction 18 becomes equilibrated at the highest temperatures explored in this study. As a consequence, experiments had to be limited to about 420 K where the concentration ratio $[CH_2$=$CHCH_2O_2]/[CH_2$=$CHCH_2]$ was equal to or greater than 50 for the highest oxygen concentrations
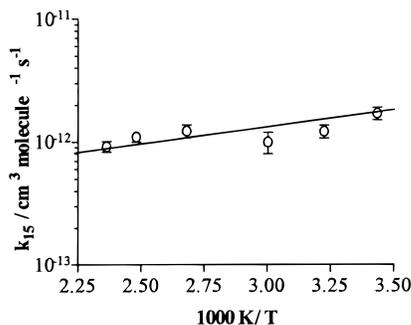
Figure 2. Arrhenius plot for the rate constant k_{15} of the cross reaction of $CH_2=CHCH_2O_2$ with CH_3O_2.

TABLE 2: Absorption Cross Sections at 235 nm ($10^{18}\sigma/cm^2$ molecule^{-1})

T/K	HO$_2$[a]	CH$_3$O$_2$[a]	CH$_2$=CHCH$_2$O$_2$[b]	H$_2$O$_2$[c]
291	1.79	4.60	6.17	0.15
310	1.80	4.56	6.17[d]	0.15[d]
333	1.81	4.51	6.17[d]	0.15[d]
373	1.82	4.40	6.17[d]	0.15[d]
403	1.84	4.32	6.17[d]	0.15[d]
423	1.85	4.27	6.17[d]	0.15[d]

[a] Taken from ref 20. [b] Taken from ref 18. [c] Taken from ref 21. [d] Assumed independent of temperature.

TABLE 3: Experimental Values of the Rate Constant for the CH$_2$=CHCH$_2$O$_2$ + CH$_3$O$_2$ Reaction

T/K	no. of determinations	k_{15}[a]/10^{-12} cm^3 molecule^{-1} s^{-1}
291	15	1.71 ± 0.20
310	2	1.22 ± 0.15
333	2	1.00 ± 0.20
373	2	1.23 ± 0.15
403	2	1.10 ± 0.10
423	2	0.91 ± 0.09

[a] Errors are based only on experimental scatter. See text for details.

that could be used without producing significant ozone concentrations, *i.e.*, $\sim 7 \times 10^{17}$ molecule cm^{-3}.

Figure 1 shows a typical decay trace obtained at room temperature along with the results of numerical simulations (smooth lines). All the parameters used in simulations were well established in the literature and are presented in Tables 1 and 2, with the exception of the branching ratio $\alpha_c = k_{15a}/k_{15}$. As mentioned above, α_c was taken as the average of the self-reaction branching ratios, *i.e.*, $\alpha(CH_3O_2) = 0.33$,[1,2] α-$(CH_2=CHCH_2O_2) = 0.61$,[18] giving $\alpha_c = 0.47$ at room temperature and assumed to increase with temperature (up to 0.66 at 420 K), assuming a temperature dependence similar to that of $\alpha(CH_3O_2)$.[1,2]

The average optimized values of k_{15} obtained are presented as a function of temperature in Table 3. Figure 2 shows the variation of k_{15} with temperature in Arrhenius form, yielding the following rate expression:

$$k_{15} = (2.8 \pm 0.7) \times 10^{-13} \times$$
$$\exp[(515 \pm 75)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \ (T = 291-423 \text{ K})$$

and where the quoted uncertainties represent statistical errors (1σ) alone.

Although the rate constant k_{15} was extracted from a relatively complex chemical system, it was essential to quantify its sensitivity to the parameters used for analysis, and a systematic analysis of propagation of errors was thus carried out as described previously.[13] Artificial decay traces were generated with the same rate constants, initial radical concentrations, and

TABLE 4: Sensitivity Parameters S_{ij}[a] for the Rate Constant of the CH$_2$=CHCH$_2$O$_2$ + CH$_3$O$_2$ Cross Reaction

a_i	$\Delta a_i/a_i$ %	$\Delta k_{15}/k_{15}$ %	S_{ij}
$\sigma(CH_2=CHCH_2O_2)$	±15	±8	0.53
$\sigma(CH_3O_2)$	±10	±9	0.90
$k(CH_3O_2 + HO_2)$	±15	±2	−0.13
$k(CH_2=CHCH_2O_2 + HO_2)$	±25	±2	−0.08
$k(CH_3O_2 + CH_3O_2)$	±10	±2	−0.20
$k(CH_2=CHCH_2O_2 + CH_2=CHCH_2O_2)$	±20	±5	−0.25
α_c	±30	±8	−0.27

[a] $S_{ij} = (\Delta k/k)/(\Delta a_i/a_i)$, where a_i refers to the analysis parameter. Fractional change in k_{15} is given by the fractional change in the analysis parameter multiplied by the appropriate sensitivity coefficient.
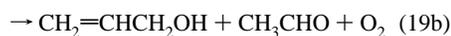
absorption cross sections employed in the analysis (see Tables 1−3). They were analyzed in the same manner as the experimental traces except for varying the most important analysis parameters of those in Tables 1−3 by 10−30% (depending on the uncertainty on the parameter) and noting the change in the value of the cross-reaction rate constant returned by the data analysis program. The results for the allylperoxy radical are presented in Table 4. It is clear that the cross-reaction rate constant is particularly sensitive in this case to σ-$(CH_2=CHCH_2O_2)$, $\sigma(CH_3O_2)$, the branching ratio α_c, and, to a lesser extent, the corresponding self-reaction rate constants. Allowing for errors of approximately 15% in $\sigma(CH_2=CHCH_2O_2)$ and 10% in $\sigma(CH_3O_2)$ resulted in a variation of 8% and 9%, respectively, in $k_{15}(CH_2=CHCH_2O_2 + CH_3O_2)$. This relative sensitivity can be explained by the fact that most of the experiments were performed at 235 nm, a wavelength that corresponds to the maximum of the UV absorption of the allyl- and methylperoxy radicals and where the signal-to-noise ratio was maximum. Hence, the error in $\sigma(HO_2)$ has less influence on the shape of the decay traces, since it absorbs more at lower wavelengths.[1,2] Reasonable variations of 15% in the rate constant of the reaction of CH_3O_2 with HO_2 and of 25% in that of the corresponding reaction of $CH_2=CHCH_2O_2$ result respectively in only <5% in k_{15}. The sensitivity of the fit to $k(HO_2 + HO_2)$ was negligible under all experimental conditions. A variation of 30% in the branching ratio α_c results in a variation of 8% in the cross-reaction rate constant. Lastly, allowing for errors of approximately 10% in $k(CH_3O_2 + CH_3O_2)$ and of 20% in $k(CH_2=CHCH_2O_2 + CH_2=CHCH_2O_2)$ resulted in a variation of 2% and 5%, respectively, in k_{15}, which was comparatively small, since in this case the cross reaction 15 was faster than the respective peroxy radicals self-reactions: $k_{15} = 1.70 \times 10^{-12}$ compared to the self-reaction rate constants 3.7×10^{-13} and 7.4×10^{-13} cm^3 molecule^{-1} s^{-1} for CH_3O_2 and $CH_2=CHCH_2O_2$, respectively, at 298 K.[1,2,10] In most cases, where the cross-reaction rate constant is between those of the self-reactions, the effects of such uncertainties are higher, at around 10−15%.

All the uncertainties described above are combined in a global systematic uncertainty of 15−20% on the cross-reaction rate constant, yielding an overall uncertainty of 30−40% (according to the temperature) on inclusion of the experimental statistical errors (1σ). A typical decay showing the sensitivity of the cross-reaction rate constant is presented Figure 1 (dashed lines correspond to variations of k_{15} in simulations of ±40%). Because of these uncertainties, there is no clear trend in the variation of k_{15} with temperature, but the Arrhenius plot suggests a small negative dependence that is consistent with all other self-reactions of primary peroxy radicals.[1,2]
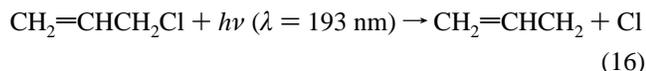
All other studies of cross-reaction rate constants, which will now be discussed, were only determined at 298 K.

In addition to the study of reaction 15, a few experiments have been performed to measure the rate constant of the cross

reaction between the allylperoxy radical and C$_2$H$_5$O$_2$:

$$CH_2=CHCH_2O_2 +$$
$$C_2H_5O_2 \rightarrow CH_2=CHCH_2O + C_2H_5O + O_2 \qquad (19a)$$

$$\rightarrow CH_2=CHCH_2OH + CH_3CHO + O_2 \quad (19b)$$

$$\rightarrow CH_2=CHCHO + C_2H_5OH + O_2 \qquad (19c)$$

The allylperoxy radical and C$_2$H$_5$O$_2$ were also generated by laser photolysis of allyl chloride at 193 nm in the presence of excess ethane and oxygen:

$$CH_2=CHCH_2Cl + h\nu \; (\lambda = 193 \text{ nm}) \rightarrow CH_2=CHCH_2 + Cl$$
$$(16)$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \qquad (20)$$

with $k_{20} = 5.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.[16]

Concentrations of allyl chloride were maintained in the range 8×10^{14} to 10×10^{14} molecule cm^{-3} corresponding to an absorption of the laser beam of between 20 and 30%. The concentration of ethane was high enough ($(1.6-3.2) \times 10^{17}$ molecule cm^{-3}) to avoid chlorine atoms reacting with CH$_2$=CHCH$_2$Cl and hence ensuing stochiometric conversion into ethyl radicals. As previously, the oxygen concentration was limited to $(3.2-4.9) \times 10^{17}$ molecule cm^{-3}.
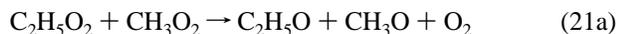
The reaction mechanism employed for analysis was similar to that used in the reaction of allylperoxy radical with CH$_3$O$_2$, the branching ratio α_c being taken as the average of the self-reaction branching ratios for CH$_2$=CHCH$_2$O$_2$ and C$_2$H$_5$O$_2$ radicals, *i.e.,* 0.61[18] and 0.63,[1,2] respectively. A small residual absorption, which could not be completely accounted for by the individual absorptions of the products, indicates that a small amount of species other than those expected may be produced by the photolytic system used for radical generation.

Fifteen experiments were performed, and the average optimized value of k_{19} obtained was

$$k_{19} = (1.0 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

The quoted uncertainties only represent statistical errors (1σ), and a study of error propagation similar to that described before results in an overall uncertainty of 55%, taking into account the small deviation in the fitting of decay traces. As for CH$_3$O$_2$, the rate constant k_{19} is higher than the self-reaction rate constants for CH$_2$=CHCH$_2$O$_2$ and C$_2$H$_5$O$_2$ radicals (7.3×10^{-13} and 7.0×10^{-14} cm^3 molecule^{-1} s^{-1}, respectively)[10,22] but is lower, by less than a factor of 2, than the cross-reaction rate constant of the allylperoxy radical with CH$_3$O$_2$ determined before.

Reaction of the Ethylperoxy Radical with CH$_3$O$_2$.

$$C_2H_5O_2 + CH_3O_2 \rightarrow C_2H_5O + CH_3O + O_2 \qquad (21a)$$

$$\rightarrow C_2H_5OH + CH_2O + O_2 \qquad (21b)$$

$$\rightarrow CH_3CHO + CH_3OH + O_2 \qquad (21c)$$

The complete reaction mechanism used in the simulations was similar to that of the allylperoxy radical (Table 1) and based on preceding studies of self-reactions.[1,2,10,18,22,23] Two different methods of radical generation were used for this study: the laser photolysis of C$_2$H$_5$Cl in the presence of CH$_4$ and the laser photolysis of CH$_3$Cl in the presence of C$_2$H$_6$. Both methods yielded the same values of k_{21} within 20%, but most experiments were performed using the latter system, since the faster reaction of Cl atoms with ethane than with methane made it easier to

scavenge Cl atoms and to avoid undesired reactions.

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl \qquad (12)$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5 \qquad (20)$$
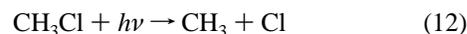
followed by the reactions of the alkyl radicals with oxygen.

The experimental conditions were as follows (molecule cm^{-3}): [CH$_3$Cl] = 4×10^{16} to 6×10^{16}, [C$_2$H$_6$] = 3×10^{17} to 4×10^{17}, [O$_2$] = 3×10^{17}, carrier gas N$_2$, total pressure = 1 atm, $T = 298$ K. The self-reaction of the ethylperoxy radical has been studied in detail,[1,2,22,23] and the room-temperature branching ratios α for the nonterminating channels are 0.63 and 0.33 for the C$_2$H$_5$O$_2$ and CH$_3$O$_2$ self-reactions, respectively. Therefore, as explained above, we have set $\alpha_c = 0.48$ for the cross reaction, the average of the above values.

Six determinations of k_{21} were performed using the experimental conditions described above, which resulted in the following rate constant:

$$k_{21} = (2.0 \pm 0.5) \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

and where the quoted uncertainties again only represent statistical errors (1σ). This value is between those of the respective self-reactions (3.7×10^{-13} and 0.70×10^{-13} cm^3 molecule^{-1} s^{-1} for CH$_3$O$_2$ and C$_2$H$_5$O$_2$ radicals, respectively). A study of error propagation similar to that described for the case of the allylperoxy radical cross reaction with CH$_3$O$_2$ results in an overall uncertainty of 41% for k_{21}.
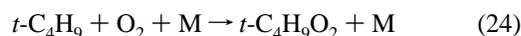
Reactions of the Neopentylperoxy Radical with CH$_3$O$_2$ and C$_2$H$_5$O$_2$. The following channels are expected for the reaction with CH$_3$O$_2$:

$$neo\text{-}C_5H_{11}O_2 +$$
$$CH_3O_2 \rightarrow neo\text{-}C_5H_{11}O + CH_3O + O_2 \qquad (22a)$$

$$\rightarrow C_5H_{11}OH + CH_2O + O_2 \qquad (22b)$$

$$\rightarrow tert\text{-}butyl\text{-}CHO + CH_3OH + O_2 \quad (22c)$$
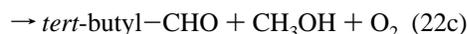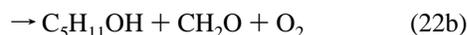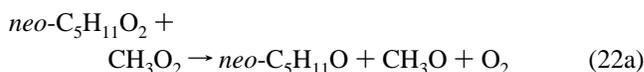
As in the preceding case, the neopentylperoxy radical and CH$_3$O$_2$ were generated by two different methods: the laser photolysis of chloromethane at 193 nm in the presence of neopentane and the flash photolysis of Cl$_2$ in the presence of methane and neopentane. Even though both methods gave the same results for the kinetics, taking into account uncertainties, the first process was preferred, since it yields equal initial concentrations of neo-C$_5$H$_{11}$O$_2$ and CH$_3$O$_2$.

The concentration of chloromethane was maintained at around 5×10^{16} molecule cm^{-3} to absorb 20–30% of the laser beam. The concentration of neopentane was *ca.* 3.0×10^{16} molecule cm^{-3}, to scavenge all chlorine atoms (k(Cl + neopentane) = 1.16×10^{-10} cm^3 molecule^{-1} s^{-1}),[16] and the oxygen partial pressure was maintained at around 10 Torr.

The reaction mechanism used was based on that determined for the self-reaction of the neopentylperoxy radical[24,25] and it is more complex than in previous cases, since the neopentoxy radical decomposes readily under the conditions of low oxygen concentration, leading to the formation of the *tert*-butylperoxy radical:

$$neo\text{-}C_5H_{11}O + M \rightarrow t\text{-}C_4H_9 + CH_2O + M \qquad (23)$$

$$t\text{-}C_4H_9 + O_2 + M \rightarrow t\text{-}C_4H_9O_2 + M \qquad (24)$$

As a result, an apparent residual absorption was observed that corresponded to the absorption of the t-C$_4$H$_9$O$_2$ radical (the
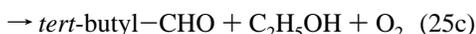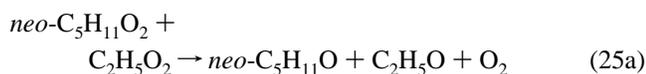
self-reaction of which is very slow).[1,2] We took into account all self- and cross reactions of t-$C_4H_9O_2$ radicals, including those with HO_2, assuming their rate constant to be equal to those of other similar peroxy radicals with HO_2 (1.5×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K).[1,2] The kinetics and mechanism of the reaction between t-$C_4H_9O_2$ and CH_3O_2 have been already investigated, yielding $k = 3.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} and $\alpha_c = 0.13$ at 298 K.[1,2] The branching ratio α of the *neo*-$C_5H_{11}O_2$ radical self-reaction has been reported as equal to 0.39,[1,2] yielding an estimated α_c of 0.36 for reaction 22.

Seven experiments were performed under the conditions described above, resulting in the following value of the rate constant:

$$k_{22} = (1.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

This value is very close to that of the neopentylperoxy self-reaction (1.2×10^{-12} cm^3 molecule^{-1} s^{-1}).[1,2] The quoted uncertainties only represent statistical errors (1σ), and the study of error propagation results in an overall uncertainty of 52%.

The cross reaction between the neopentylperoxy radical and $C_2H_5O_2$

$$neo\text{-}C_5H_{11}O_2 +$$
$$C_2H_5O_2 \rightarrow neo\text{-}C_5H_{11}O + C_2H_5O + O_2 \quad (25a)$$
$$\rightarrow C_5H_{11}OH + CH_3CHO + O_2 \quad (25b)$$
$$\rightarrow tert\text{-butyl}-CHO + C_2H_5OH + O_2 \quad (25c)$$

was investigated using the flash photolysis of molecular chlorine in the presence of neopentane and ethane: $[C_5H_{12}] = 3.2 \times 10^{16}$ and $[C_2H_6] = 6.5 \times 10^{16}$ (units of molecule cm^{-3}). Synthetic air (to 1 atm) was the carrier gas.

The chemical system was similar to that used above for reaction 22, and the average of seven measurements (using $\alpha_c = 0.51$) yields

$$k_{25} = (5.6 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

The global uncertainty was estimated to be about 38%. Note that the cross-reaction rate constant is between the values for $C_2H_5O_2$ and neo-$C_5H_{11}O_2$ self-reactions.

Reactions of the Cyclohexylperoxy Radical with CH_3O_2 and $C_2H_5O_2$. The expected reaction channels of the reaction with CH_3O_2 are

$$c\text{-}C_6H_{11}O_2 + CH_3O_2 \rightarrow c\text{-}C_6H_{11}O + CH_3O + O_2 \quad (26a)$$
$$\rightarrow c\text{-}C_6H_{11}OH + CH_2O + O_2 \quad (26b)$$
$$\rightarrow c\text{-}C_6H_{10}O + CH_3OH + O_2 \quad (26c)$$

This is an example of a cross reaction between CH_3O_2 and a secondary peroxy radical that exhibits a slow self-reaction ($k = 4.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}).[26]

The cyclohexyl- and methylperoxy radicals were generated using the flash photolysis of Cl_2 in the presence of cyclohexane and methane in appropriate concentrations (molecule cm^{-3}): $[CH_4] = (4.5-10) \times 10^{18}$; $[O_2] = (1.5-2.0) \times 10^{19}$. The concentration of C_6H_{12} was again chosen to ensure that all chlorine atoms were stoichiometrically converted into cyclohexyl radicals ($k(Cl + C_6H_{12}) = 2.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},[16] $[C_6H_{12}] = (2-4) \times 10^{15}$ molecule cm^{-3}).

The kinetics and mechanism of the self-reaction of the cyclohexylperoxy radical have already been studied in detail

in our laboratory,[26,27] and the principal difference to the previous analysis mechanism was that the alkoxy radical c-$C_6H_{11}O$ could undergo ring-opening at low oxygen partial pressure (below 600 Torr) instead of reacting with O_2 to form HO_2 and cyclohexanone:[26,27]

$$c\text{-}C_6H_{11}O + M \rightarrow CH_2(CH_2)_4CHO + M \quad (27)$$
$$c\text{-}C_6H_{11}O + O_2 \rightarrow c\text{-}C_6H_{10}O + HO_2 \quad (28)$$

Reaction 27 becomes significant for oxygen partial pressures below 150 Torr,[26,27] yielding a more complex chemical mechanism with an observed rate constant k_{26} that depends upon the oxygen concentration ($k_{26} = (3-9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for $[O_2] = 10-700$ Torr). Consequently, experiments were performed here under high oxygen concentrations so that reaction 27 could be neglected.[26,27] The branching ratio of the self-reaction of the c-$C_6H_{11}O_2$ radical has been previously measured as 0.29, yielding an estimated α_c of 0.31.

The average of 12 runs yields the following value for k_{26}:

$$k_{26} = (9.0 \pm 0.15) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

where once again the quoted uncertainties represent statistical errors (1σ) alone. The global uncertainty is estimated to be about 35%.

The cross reaction with $C_2H_5O_2$

$$c\text{-}C_6H_{11}O_2 + C_2H_5O_2 \rightarrow c\text{-}C_6H_{11}O + C_2H_5O + O_2 \quad (29a)$$
$$\rightarrow c\text{-}C_6H_{11}OH + CH_3CHO + O_2 \quad (29b)$$
$$\rightarrow c\text{-}C_6H_{10}O + C_2H_5OH + O_2 \quad (29c)$$

was studied using the flash photolysis apparatus, where radicals were generated by the photolysis of molecular chlorine in the presence of c-C_6H_{12}, C_2H_6, and oxygen: $[c$-$C_6H_{12}] = 3.3 \times 10^{16}$ molecule cm^{-3} and $[C_2H_6] = 1.45 \times 10^{17}$ molecule cm^{-3} in oxygen (to 1 atm), yielding similar radical concentrations of each peroxy radical. The analysis system was the same as above, and six experiments resulted in the following value for k_{29}, using $\alpha_c = 0.46$ as the average of the respective branching ratios of 0.63 and 0.29 for the $C_2H_5O_2$ and c-$C_6H_{11}O_2$ self-reactions:

$$k_{29} = (4.0 \pm 0.2) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

The study of the propagation of errors results in an overall uncertainty of 37%.

Note that the rate constant is not significantly different from that of the c-$C_6H_{11}O_2$ self-reaction and about a factor of 2 lower than the corresponding cross-reaction rate constant with CH_3O_2 determined above.

Reaction of the Benzylperoxy Radical with CH_3O_2.

$$C_6H_5CH_2O_2 + CH_3O_2 \rightarrow C_6H_5CH_2O + CH_3O + O_2 \quad (30a)$$
$$\rightarrow C_6H_5CHO + CH_3OH + O_2 \quad (30b)$$
$$\rightarrow C_6H_5CH_2OH + CH_2O + O_2 \quad (30c)$$

The benzylperoxy radical was selected as an example of a radical bearing an aromatic substituent and that exhibits a fast self-reaction ($k = 7.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K).[11]

The benzyl- and methylperoxy radicals were generated by flash photolysis of Cl_2 in the presence of appropriate concentrations of toluene and methane. The concentration of toluene was

CH$_3$O$_2$ and C$_2$H$_5$O$_2$

J. Phys. Chem., Vol. 100, No. 34, 1996 **14379**

about 5 × 10^{15} molecule cm^{-3} (k(Cl + toluene) = 6.1 × 10^{-11} cm^3 molecule^{-1} s^{-1}),[11] which was measured by its absorption at 250 nm (σ = 0.37 × 10^{-18} cm^2 molecule^{-1}),[28] while the methane partial pressure was fixed at 100 Torr. Under such conditions, approximately equal concentrations of both radicals were generated. The self-reaction of the benzylperoxy radical has been studied in detail,[11] and the corresponding branching ratio has been reported as 0.40 yielding α_c = 0.36.

Fifteen experiments were performed under the conditions described before with most analyses yielding values of k_{30} between 1 × 10^{-12} and 2 × 10^{-12} cm^3 molecule^{-1} s^{-1}. However, the sensitivity analysis indicated that acceptable fits to decay curves could still be obtained with much lower values so that in this particular case, only an upper limit for the rate constant can be given:

$$k_{30} < 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

This value is significantly lower than the rate constant of the benzylperoxy radical self-reaction.[11] This is in contrast to the other cross reactions investigated, where the cross-reaction rate constant is found to be close to that of the RO$_2$ self-reaction. It should be pointed out that measurements were fairly difficult in the case of this particular reaction as a result of the formation of the highly absorbing benzaldehyde as a product. Consequently, uncertainties were higher in this case than for the other cross reactions studied.
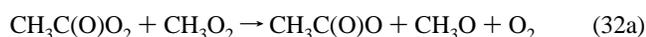
Reaction of the Chloromethylperoxy Radical with CH$_3$O$_2$.

$$CH_2ClO_2 + CH_3O_2 \rightarrow CH_2ClO + CH_3O + O_2 \quad (31a)$$

$$\rightarrow CH_2ClOH + CH_2O + O_2 \quad (31b)$$

$$\rightarrow HC(O)Cl + CH_3OH + O_2 \quad (31c)$$

For this reaction between CH$_3$O$_2$ and a halogenated peroxy radical, the laser photolysis of dichloromethane in the presence of methane was used to generate simultaneously the chloromethyl- and methylperoxy radicals in equal concentrations. It was assumed that the photolysis of CH$_2$Cl$_2$ at 193 nm resulted mainly in the formation of CH$_2$Cl and Cl atoms.[29] The dichloromethane concentration was fixed at around 5 × 10^{15} molecule cm^{-3} (k(Cl + CH$_2$Cl$_2$) = 3.3 × 10^{-13} cm^3 molecule^{-1} s^{-1}),[15] while the partial pressures of methane and oxygen were equal to 100 and 15 Torr, respectively. The kinetics and mechanism of the self-reaction of CH$_2$ClO$_2$ radicals have been already investigated,[12,30] yielding a branching ratio equal to nearly 1. Hence, by use of α_c = 0.66, the following rate constant was obtained from the six analysis of experiments:

$$k_{31} = (2.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

a value close to that of the CH$_2$ClO$_2$ self-reaction (3.7 × 10^{-12} cm^3 molecule^{-1} s^{-1}).[12]

The quoted uncertainties only represent statistical errors (1σ), and the study of error propagation results in an overall uncertainty of about 40%.

Reactions of the Acetylperoxy Radical with CH$_3$O$_2$ and C$_2$H$_5$O$_2$.

$$CH_3C(O)O_2 + CH_3O_2 \rightarrow CH_3C(O)O + CH_3O + O_2 \quad (32a)$$

$$\rightarrow CH_3C(O)OH + CH_2O + O_2 \quad (32b)$$

The acetylperoxy radical is the simplest example of the class of acylperoxy radicals, and all its reactions with radical species are known to be fast.[1,2]

The rate constant of the cross reaction of the acetylperoxy radical with CH$_3$O$_2$ has already been estimated as part of the investigation of the CH$_3$C(O)O$_2$ self-reaction, CH$_3$O$_2$ being produced in secondary reactions,[5] since the acetoxy radicals CH$_3$C(O)O formed in channel 32a are unstable and yield methyl radicals that are rapidly converted into methylperoxy radicals:

$$CH_3C(O)O + M \rightarrow CH_3 + CO_2 + M \quad (33)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (10)$$
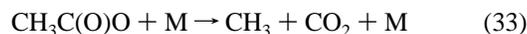
The cross reaction has also been found to be fast with k_{32} = 1.3 × 10^{-11} cm^3 molecule^{-1} s^{-1}.[1,2] In the present work, and in a very recent work,[31] the reaction was reinvestigated by generating CH$_3$O$_2$ simultaneously with CH$_3$C(O)O$_2$. The conventional flash photolysis of Cl$_2$ in the presence of acetaldehyde and methane was used for this particular study to generate the acetyl- and methylperoxy radicals. The experimental conditions were (concentrations in units of molecule cm^{-3}) [CH$_3$CHO] = (4−5) × 10^{15} (k(Cl + CH$_3$CHO) = 7.6 × 10^{-11} cm^3 molecule^{-1} s^{-1}),[16] [CH$_4$] = (3.5−4.0) × 10^{18}, [O$_2$] = (4.5−5.0) × 10^{18}, and [Cl$_2$] = (4.5−5.0) × 10^{16} and resulted in radical concentrations between 5.2 × 10^{13} and 7.5 × 10^{13} molecule cm^{-3}. Since acetylperoxy radicals have no α hydrogen, there are only two possible channels for the cross reaction 32; the previous studies of acetylperoxy radicals kinetics proposed different branching ratios for reactions 32a and 32b, varying from α_c = 0.47 to α_c = 0.83 at room temperature.[5,31] Data analyses undertaken to estimate the sensitivity to the branching ratio α_c of the cross-reaction rate constant k_{32} show that k_{32} never varies by more than 15% upon varying α_c between 0.5 and 1. Thus, the proposed value for α_c is the average of the self-reaction branching ratios for CH$_3$C(O)O$_2$ and CH$_3$O$_2$, *i.e.*, α_c = 0.65, which also corresponds to the average of the two branching ratios determined experimentally.[5,31]

The results of five experiments yield the following rate constant:

$$k_{32} = (8.2 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

and confirm that the reaction is fast and that the rate constant is closer to that of the acetylperoxy self-reaction (1.5 × 10^{-11} cm^3 molecule^{-1} s^{-1})[31] than to that of CH$_3$O$_2$ (3.7 × 10^{-13} cm^3 molecule^{-1} s^{-1}).[1,2] A similar study of error propagation as described for the case of the allylperoxy radical results in an overall uncertainty of 42%.

The present result is in agreement within experimental uncertainties with previous determinations and particularly with the recent work of Roehl *et al.*[31] who report k_{32} = (9.8 ± 2.0) × 10^{-12} cm^3 molecule^{-1} s^{-1} at room temperature. Considering all determinations and giving more weight to the measurements in which CH$_3$O$_2$ and CH$_3$C(O)O$_2$ were generated simultaneously (present work and Roehl *et al.*[31]), we propose k_{32} = (9.5 ± 2.0) × 10^{-12} cm^3 molecule^{-1} s^{-1}.

In addition to the study of reaction 32, the rate constant of the cross reaction between the acetylperoxy radical and C$_2$H$_5$O$_2$,

$$CH_3C(O)O_2 + C_2H_5O_2 \rightarrow CH_3C(O)O + C_2H_5O + O_2 \quad (34a)$$

$$\rightarrow CH_3C(O)OH + CH_3CHO + O_2 \quad (34b)$$

was measured in a way similar to that for CH$_3$O$_2$. The acetylperoxy radical and C$_2$H$_5$O$_2$ were generated by the flash

TABLE 5: Rate Constants at 298 K for RO$_2$ + CH$_3$O$_2$ and RO$_2$ + C$_2$H$_5$O$_2$ Cross Reactions Compared to Those for the RO$_2$ Self-Reaction

RO$_2$	10^{13}k(RO$_2$ + CH$_3$O$_2$)^a cm^3 molecule^{-1} s^{-1}	10^{13}k(RO$_2$ + C$_2$H$_5$O$_2$)^a cm^3 molecule^{-1} s^{-1}	10^{13}k(RO$_2$ + RO$_2$) cm^3 molecule^{-1} s^{-1}
CH$_3$O$_2$		2.0^b (3.2)	3.7^e
CH$_2$=CHCH$_2$O$_2$	17^b (10)	10^b (4.5)	7.3^g
C$_2$H$_5$O$_2$	2.0^b (3.2)		0.70^e
neo-C$_5$H$_{11}$O$_2$	15^b (13)	5.6^b (5.8)	12^e
c-C$_6$H$_{11}$O$_2$	0.9^b (2.5)	0.4^b (1.1)	0.42^e
C$_6$H$_5$CH$_2$O$_2$	<20^b (34)		77^h
CH$_2$ClO$_2$	25^b (23)		37^i
CH$_3$C(O)O$_2$	95^{b,c} (47)	100^b (20)	150^j
CH$_3$C(O)CH$_2$O$_2$	38^d (34)		80^d
t-C$_4$H$_9$O$_2$	0.031^e (0.066)	see text	0.00030^e
CCl$_3$O$_2$	66^f (24)		40^f

^{a}Values in parentheses calculated using expression I. ^{b}This work. ^{c}The determined value in this work is 8.2 × 10^{-12} cm^3 molecule^{-1} s^{-1}, but the proposed value also takes into account other determinations (see text). ^{d}Taken from ref 6. ^{e}Taken from ref 1. ^{f}Taken from ref 9. ^{g}Taken from ref 10. ^{h}Taken from ref 11. ^{i}Taken from ref 12. ^{j}Taken from ref 31.

photolysis of Cl$_2$ in the presence of acetaldehyde, ethane, and synthetic air in the following concentrations (in molecule cm^{-3}): [Cl$_2$] = 5 × 10^{16}, [CH$_3$CHO] = 1.6 × 10^{16}, and [C$_2$H$_6$] = 2.2 × 10^{16} in 1 atm synthetic air. The reaction mechanism is more complex than the previous one used for the reaction between CH$_3$C(O)O$_2$ and CH$_3$O$_2$, here now being four peroxy radicals present (CH$_3$O$_2$ being formed, as seen above, by the CH$_3$C-(O)O radical decomposition). Taking into account all peroxy radicals interactions, and by use of a branching ratio α$_c$ = (1 + 0.63)/2 = 0.82, the following rate constant was obtained as an average of the results of three experiments:

$$k_{34} = (1.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at 298 K}$$

This value is close to that of the cross reaction of CH$_3$C(O)-O$_2$ with CH$_3$O$_2$ and to that of the acetylperoxy self-reaction. The study of error propagation accounting for statistical and systematic errors results in an overall uncertainty of 54%.

The reactions of CH$_3$C(O)O$_2$ with other RO$_2$ radicals all seem fast, and further work is in progress in order to verify whether this is true, irrespective of the nature of the RO$_2$.

Discussion

Accuracy of Results. Several factors influence the accuracy of the results, as described above in the particular case of the CH$_2$=CHCH$_2$O$_2$ + CH$_3$O$_2$ reaction, where we were particularly concerned with the reaction mechanism used in the simulation of experimental decay traces. The chemistry associated with peroxy radical cross reactions is too complicated for a reliable determination of the yield of reaction products. Thus, the chemical mechanisms used in the analysis of kinetics were derived from those previously determined for the self-reactions of the two reacting radicals, the principal uncertainty being on the value of the branching ratio α$_c$ for the nonterminating channel of the cross reaction, which was unknown. This parameter was assumed to be equal to the arithmetic average of the branching ratios of self-reactions, and as in the case of the allylperoxy radical reaction discussed above, it was shown that the error on the cross reaction rate constant resulting from the uncertainty on α$_c$ was fairly small, less than 15% for all the reactions investigated.

The sensitivity analysis has shown that the principal factors influencing the results were the UV absorption cross sections of the peroxy radicals and their self-reaction rate constants (particularly the larger rate constant). Most of those parameters used in the determination procedure of cross-reaction rate constants are fairly well-known, with uncertainties ranging from 10 to 20%. The analysis of error propagation, taking into account all uncertainties, resulted in a global systematic uncertainty of 15−30% on the cross-reaction rate constant, yielding an overall uncertainty of 30−60%, including the experimental statistical errors (1σ). It must be recognized that this estimation of uncertainties does not take into account any unknowns in the reaction mechanism (apart from the branching ratio α$_c$). However, the extrapolation of the well-known reaction mechanism prevailing in the corresponding radical self-reactions is reasonable. Good indications in favor of this assumption were obtained previously in mechanistic studies of the reactions of the acetylperoxy[5] and acetonylperoxy[6] radicals. Considering all the possible sources of errors, we estimate that the total uncertainty should, in any case, be smaller than a factor of 2. In the particular case of the reaction of allylperoxy radicals with C$_2$H$_5$O$_2$, where slight deviations remained in the fitting of decay traces, by simulating using the expected reaction mechanism, the uncertainty was increased accordingly, as indicated above in the presentation of results.

Cross reactions between two radicals are generally difficult to investigate, and therefore, fairly large uncertainties are expected in the determination of the rate constant of such processes. Nevertheless, the above analysis of errors shows that the kinetic data determined in this work are significant and reliable enough to be used for establishing trends in reactivity for various types of cross reaction. It should be pointed out that this has been possible because the cross reaction rate constant is generally closer to the larger self-reaction rate constant of the two radicals, as discussed below, and it is only under this condition that the global kinetics exhibit good enough sensitivity to the cross-reaction rate parameters. As seen above, the benzylperoxy case was an exception to the rule and thus only an upper limit could be determined for the corresponding cross-reaction rate constant.

Analysis of Results. The values of the rate constants available to date for peroxy radical cross reactions with CH$_3$O$_2$ and C$_2$H$_5$O$_2$ radicals are reported in Table 5. Also included are the rate constants of corresponding peroxy radical self-reactions for comparison. The rate constants for the reactions of C$_2$H$_5$O$_2$, CH$_2$=CHCH$_2$O$_2$, *neo*-C$_5$H$_{11}$O$_2$, *c*-C$_6$H$_{11}$O$_2$, C$_6$H$_5$-CH$_2$O$_2$, and CH$_2$ClO$_2$ with CH$_3$O$_2$ and those of all cross reactions involving C$_2$H$_5$O$_2$ are presented for the first time in the present work. The rate constant for the CH$_3$C(O)O$_2$ + CH$_3$O$_2$ reaction, which has already been reported in the literature,[5] was reinvestigated simultaneously in the present study and by Roehl *et al.*,[31] the three determinations being in good agreement.

The cross reactions of CH$_3$C(O)CH$_2$O$_2$, t-C$_4$H$_9$O$_2$, and CCl$_3$O$_2$ with CH$_3$O$_2$ were derived from previous work and are now briefly evaluated.

CH$_3$C(O)CH$_2$O$_2$. The cross reaction of the acetonylperoxy radical with CH$_3$O$_2$ was investigated by Bridier et al.[6] at room temperature using the flash photolysis of Cl$_2$ in the presence of acetone, methane, and oxygen. The chemistry in this system is complicated by the formation of acetylperoxy radicals from the decomposition of the acetoxy radical, CH$_3$C(O)CH$_2$O. Taking account of all peroxy radicals interactions in the chemical model, Bridier et al.[6] proposed a value of $(3.8 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for the cross-reaction rate constant. This value is between the self-reaction rate constants for the acetonylperoxy and the methylperoxy radicals (8.0×10^{-12} and 3.7×10^{-13} cm^3 molecule^{-1} s^{-1}, respectively, at 298 K).[1,2,6] The value of the branching ratio α_c was determined to be (0.3 ± 0.1) compared to the average of the self-reaction branching ratios, i.e., $\alpha_c = 0.54$.

t-C$_4$H$_9$O$_2$. The reaction of the $tert$-butylperoxy radical with CH$_3$O$_2$ involves a radical bearing a tertiary central carbon atom having a very slow self-reaction: $k = 3.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.[1,2] The rate constant was studied by two groups[7,8] and was derived indirectly by modeling the observed product yields of the t-C$_4$H$_9$O$_2$ radical self-reaction in which the methylperoxy radicals were produced from the decomposition of the $tert$-butoxy radicals. The results obtained by the two groups are in significant disagreement, Parkes reporting a value of $(1.0 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K,[7] whereas Osbourne et al. propose a rate constant 2 orders of magnitude lower[8] (3.95×10^{-15} cm^3 molecule^{-1} s^{-1}). For their part, Lightfoot et al.[1] recommended 3.1×10^{-15} cm^3 molecule^{-1} s^{-1}, derived from the Arrhenius plot of the data of Osbourne et al. Note that in our study of the reaction of neo-C$_5$H$_{11}$O$_2$ with CH$_3$O$_2$ in which the t-C$_4$H$_9$O$_2$ and CH$_3$O$_2$ radicals were formed in secondary reactions,[1,2] the best fits of decay traces at long reaction times were obtained using a value of $\sim 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the cross reaction of the two latter radicals. The sensitivity to this value was, however, fairly poor.

We have performed a few experiments, within the present work, to measure the rate constant of the t-C$_4$H$_9$O$_2$ + C$_2$H$_5$O$_2$ cross reaction by laser-flash photolysis of $tert$-butyl chloride at 193 nm in the presence of ethane and oxygen (the investigation of the cross reaction with CH$_3$O$_2$ could not be studied using this method owing to the too large difference in reactivity of Cl atoms with CH$_4$ and t-C$_4$H$_9$Cl). Experimental results were not very accurate, since the shape of decay traces could not be simulated fully. Nevertheless, the measured values of the cross-reaction rate constant, ranging from 1×10^{-13} to 2×10^{-13} cm^3 molecule^{-1} s^{-1}, were found again to be much larger than the recommended value for the t-C$_4$H$_9$O$_2$ + CH$_3$O$_2$ reaction, whereas a similar value can reasonably be expected for the rate constant of both reactions. We have ignored this last determination because of the low reliability of measurements, but it confirms the large uncertainty that exists for the rate constant of the t-C$_4$H$_9$O$_2$ + CH$_3$O$_2$ cross reaction. Nevertheless, we have included in Table 5 the value recommended by Lightfoot et al.[1]

CCl$_3$O$_2$. The reaction of the trichloromethylperoxy radical with CH$_3$O$_2$ has been investigated recently in our laboratory[9] using the flash photolysis of CCl$_4$ in the presence of methane and oxygen. The reaction mechanism is fairly well established, and the measured value for the cross-reaction rate constant is $(6.6 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K. The value of this rate constant is significantly higher than k_{31}(CH$_2$ClO$_2$ + CH$_3$O$_2$) measured in this work but is still of the same order

of magnitude as the rate constant for the CCl$_3$O$_2$ radical self-reaction[9] ($k = 4.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}). The value of the branching ratio α_c was optimized in simulations and found to be equal to (0.5 ± 0.2) compared to the average of the self-reaction branching ratios, i.e., $\alpha_c = 0.66$.

Analysis of Cross Reaction Kinetics. As for peroxy radical self-reactions, the rate constants for cross reactions vary over a very wide range: more than 4 orders of magnitude from the rate constant of the t-C$_4$H$_9$O$_2$ + CH$_3$O$_2$ reaction ($k = 3.1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}) to that of the CH$_3$C(O)O$_2$ + CH$_3$O$_2$ reaction ($k \approx 10^{-11}$ cm^3 molecule^{-1} s^{-1}). To date, the temperature dependence has been measured for the cross-reaction rate constants of three radicals: CH$_2$=CHCH$_2$O$_2$ (this work), CH$_3$C(O)O$_2$,[1,2] and t-C$_4$H$_9$O$_2$.[1,2] The values of E/R are comparable to those observed for the corresponding self-reactions, being positive for the slowest reactions ($+1430$ K for the $tert$-butylperoxy radical reaction) and negative for most other reactions (-430 K for the allylperoxy radical and -272 K for the acetylperoxy radical). The best recommendation that can be made at the present time is to take for the cross reaction a temperature dependence similar to that measured for the peroxy radical self-reaction having the most comparable room-temperature rate constant to the cross reaction.

It is observed that, in most cases, the cross reaction rate constant is between the self-reaction rate constants of the two reacting radicals and is often close to that of the fastest self-reaction. Only in the cases of the reactions of CH$_3$O$_2$ with CH$_2$=CHCH$_2$O$_2$ and of CCl$_3$O$_2$ and C$_2$H$_5$O$_2$ with CH$_2$=CHCH$_2$O$_2$ is the cross reaction rate constant significantly larger than that of either self-reaction. The following relationship between cross and self-reactions of two radicals has been proposed:[3]

$$k(\text{RO}_2 + \text{R}'\text{O}_2) = 2\sqrt{k(\text{RO}_2 + \text{RO}_2) \times k(\text{R}'\text{O}_2 + \text{R}'\text{O}_2)} \quad \text{(I)}$$

and has been applied to the reactions of interest in this work. The values calculated from expression I are included (in parentheses) in Table 5. It is apparent that for most reactions, the experimental and calculated rate constant do not differ by more than a factor of 2 with the exception of the reactions of the acetylperoxy radical, which seem to be always large, and those of the $tert$-butylperoxy radical, which are small but determined with poor accuracy, as discussed above. The other exception is that of CCl$_3$O$_2$, which is larger than the predicted value by a factor of almost 3 and was determined with fairly good accuracy.[9] We have no explanation for these particular exceptions. Nevertheless, expression I may be a fairly good approximation for estimating cross-reaction rate constants of peroxy radicals, taking into account the large differences observed from one reaction to another and the fairly large uncertainties in the measurements as discussed above.

It can also be observed that rate constants of cross reactions with CH$_3$O$_2$ are often close to the rate constants of RO$_2$ self-reactions. This is particularly true for the fastest reactions, which are the most important in reaction systems. Thus, an alternative recommendation might be to take for CH$_3$O$_2$ and C$_2$H$_5$O$_2$ cross reactions a rate constant close to that of the RO$_2$ self-reaction. This would be a good approximation for fast reactions and wrong for slow reactions, but the slow reactions generally play a minor role in the reaction systems. The only exception to the second rule of interest is the CH$_3$O$_2$ + C$_6$H$_5$CH$_2$O$_2$ reaction, which is found to be slower than predicted. As already pointed out, this discrepancy may arise from large experimental uncertainties resulting from the formation of strongly absorbing benzaldehyde, which perturbs the flash photolysis study of this system.

Conclusion

We have presented in this paper the first systematic study of the rate constants of a series of cross reactions of peroxy radicals, $RO_2 + CH_3O_2$ and $RO_2 + C_2H_5O_2$, that are likely to play a significant role in the chemistry of the troposphere or in low-temperature combustion. The RO_2 radicals were chosen to represent typical classes of radicals so that general trends could be derived from the kinetic results. It has been shown that the rate constant for a given cross reaction is generally between the rate constants for the self-reactions of RO_2 and CH_3O_2 (or $C_2H_5O_2$) with a reasonable agreement with the currently accepted relationship between cross- and self-reaction rate constants (expression I). However, when the RO_2 self-reaction is fast, it seems that the cross reaction with CH_3O_2 (or $C_2H_5O_2$) is also fast with similar rate constants for both reactions. This is particularly apparent for the reactions of the acetylperoxy radical. This latter radical is also among the most abundant peroxy radicals in tropospheric and combustion reaction systems, and its measured reactions with radical species are known to be quite fast with $k \approx (1-2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The question remains as to whether this is also true for reactions of acetylperoxy with all other peroxy radicals, whatever their structure. Work is in progress to assess this question, and preliminary results suggest that the enhanced reactivity is indeed independent of the nature of R in $CH_3C(O)O_2 + RO_2$ reactions.

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