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Rate Constants for Reactions of (Perhaloalkyl)peroxyl Radicals with Alkenes in Methanol

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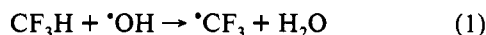
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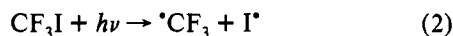
A number of halogenated peroxyl radicals were produced in methanolic solutions through the radiolytic reduction of halocarbons in the presence of oxygen. Rate constants for the reactions of these radicals with unsaturated organic compounds were measured by competition kinetics with chlorpromazine as the reference compound. The rate constants were in the range 5×10^4 to 2×10^8 L mol⁻¹ s⁻¹ and generally increased with increasing fluorine substitution on the peroxyl radical and increasing substitution of alkyl groups about the double bond in the alkene. Limits on the rate constants with increasing substitution, however, suggested an additional effect of steric hindrance. Similar results were found for the oxidation of chlorpromazine by several of these halo-peroxyl radicals.

Introduction

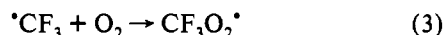
Most of the chemical compounds under consideration as possible replacements for the halons and chlorofluorocarbons (CFCs) are expected to degrade in the atmosphere, either because they contain one or more C–H bonds which are subject to attack by atmospheric hydroxyl radicals, for example,



or because they may be photodissociated in the atmosphere, for example,



The resulting carbon-centered radical will rapidly react with oxygen to produce a halogenated peroxyl radical



Subsequent reactions of the peroxyl radical lead to the removal of the halogens from the atmosphere. There is, presently, a limited amount of information on the possible atmospheric reactions of these halogenated peroxyl radicals. Peroxyl radicals generally are expected to react with NO, with NO₂, or with other peroxyl radicals, including HO₂·.² Other reactions of peroxyl radicals, for example with alkenes, generally are considered to be too slow to be of any importance in the atmosphere. Whereas this is clearly true for the nonhalogenated alkylperoxyl radicals, halogenation may increase the reactivity of these radicals sufficiently that other reaction pathways become important.

Formation and reactions of halogenated peroxyl radicals might also relate to potential physiological effects of these halocarbon replacements. For example, the toxicity of CCl₄ has been suggested to arise from reactions of CCl₃O₂·, formed after the one-electron reduction of the parent.³ These peroxyl radicals are strong oxidants and will react with antioxidants such as vitamin

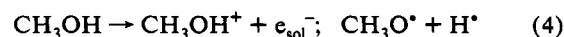
C or vitamin E, but they also may react with other physiological molecules, such as lipids, initiating damage.^{3,4}

Over the past several years, we have been engaged in the study of the liquid-phase reactivity of halogenated peroxyl radicals, primarily their electron-transfer reactions.^{5–14} These studies generally have been on the simple halogenated methylperoxyl radicals, mostly on CCl₃O₂·. Many of the possible CFC replacement compounds, however, contain halogens located on adjacent carbon atoms or contain mixed halogens. In these cases, the effect on the reactivity of the subsequent peroxyl radical might be significantly different. We have therefore measured the rate constants for the reactions of a number of these peroxyl radicals with alkenes in order to establish reactivity patterns.

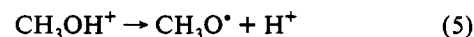
Experimental Section¹⁵

The rate constants for reactions of (perhaloalkyl)peroxyl radicals with various alkenes in methanolic solutions were determined by pulse radiolysis. Air-saturated stock solutions containing 0.5–2% halocarbon and 1×10^{-4} – 5×10^{-3} mol L⁻¹ chlorpromazine were prepared for the liquid halocarbons. For the gaseous halocarbons, mixtures were prepared by adding a halocarbon-saturated chlorpromazine solution to oxygen-saturated methanol. A fresh sample of the solution was introduced into the irradiation cell with a syringe and was irradiated under aerobic conditions with a single pulse of 2-MeV electrons, with a dose of about 10 Gy.

The irradiation of methanol by ionizing radiation results in the formation of solvated electrons, radical cations, methoxyl radicals, and hydrogen atoms.¹⁶

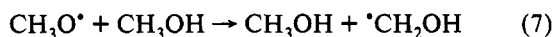
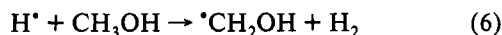


The radical cation will deprotonate,

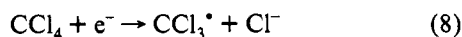


The hydrogen atom and the methoxyl radical will react with the solvent to produce the hydroxymethyl radical, with $k_6 = 2.6 \times 10^6$ L mol⁻¹ s⁻¹¹⁷ and $k_7 = 2.6 \times 10^5$ L mol⁻¹ s⁻¹¹⁸

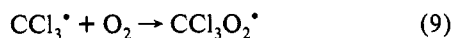
* Abstract published in *Advance ACS Abstracts*, May 1, 1994.



Halogenated alkyl radicals are produced by the reduction of chlorine-, bromine-, or iodine-containing halocarbons by the solvated electron, for example:



In the presence of oxygen, (haloalkyl)peroxyl radicals are formed rapidly, $k_9 \sim 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.⁴

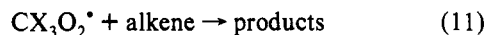


Although $\text{}^\bullet\text{CH}_2\text{OH}$ is a reducing radical, it does not react rapidly with the haloalkanes used in this study and should react with oxygen to make the alkylperoxyl radical $\text{HOCH}_2\text{O}_2^\bullet$. This radical has a much lower reactivity than the (haloalkyl)peroxyl radicals under investigation here and, therefore, does not interfere with these kinetic measurements.⁴

In our pulse-radiolysis apparatus, reactions are monitored by kinetic spectrophotometry. Peroxyl radicals absorb only in the ultraviolet, primarily below 280 nm, and this absorption is not particularly strong. The same is true of any expected products of the reaction of these radicals with alkenes. With our apparatus, measurements are difficult in this spectral region, so rather than following the reaction directly, we have determined the rate constants by competition kinetics using chlorpromazine (CIPz) as a reference. The rate of oxidation of CIPz is determined directly by following the formation of the CIPz radical at 525 nm.



The addition of alkenes to solutions of CIPz leads to competition between reaction 10 and 11.



This will result in an enhanced rate of formation and decreased yield of $\text{CIPz}^{\bullet+}$. At constant CIPz concentration, the observed rate of formation of $\text{CIPz}^{\bullet+}$ (k_{obs}) is given by

$$k_{\text{obs}} = k_0 + k_1[\text{alkene}] \quad (12)$$

where k_0 is the first-order rate constant in the absence of alkene, which includes the rate of reaction 10 and any other loss processes for the peroxyl radical except reaction 11, and k_1 is the second-order rate constant for reaction 11. The second-order rate constant is derived from the slope of a plot of the first-order rate constant against alkene concentration (Figure 1). At least three separate experiments were performed for each alkene concentration, and at least three alkene concentrations were employed for each alkene-radical reaction.

There are two major sources of uncertainty in the derived second-order rate constants: the statistical uncertainties in the first- and second-order fits and errors in the measurement of the volume of the alkene. (Any uncertainty in the halocarbon concentration or the concentration of CIPz does not affect the precision or accuracy of the alkene rate measurement.) In some cases the statistical error was quite low, only a few percent. More typically, however, the statistical error from the second-order fits was almost 10%, which we feel is more representative of the uncertainty from this source. In addition, we estimate uncertainties of 10% associated with the measurement of the alkene volume and 5% from other sources of error, including the measurement of the total volume of the solution. This results in a total estimated uncertainty in the reported rate constants of $\pm 25\%$.

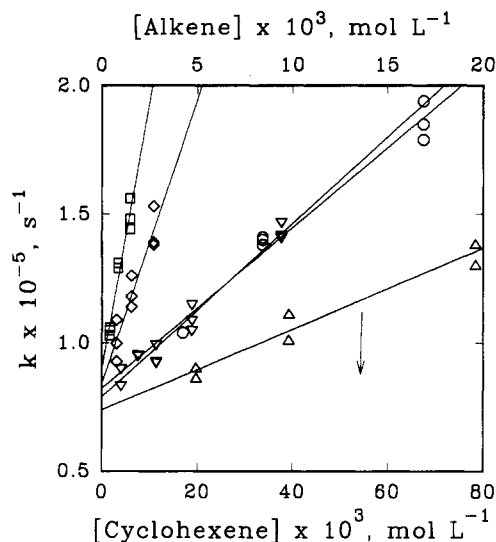


Figure 1. Plot of the first-order rate of formation of the chlorpromazine radical cation by reaction with $(\text{CF}_3)_2\text{CFO}_2^\bullet$ as a function of added alkene. Δ , cyclohexene; ∇ , 2-methyl-2-butene; \circ , 1-methylcyclohexene; \diamond , 1,2-dimethylcyclohexene; \square , 2,3-dimethyl-2-butene.

TABLE 1: Rate Constants for Reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$, $\text{CCl}_3\text{O}_2^\bullet$, and $\text{CBr}_3\text{O}_2^\bullet$ Radicals with Alkenes in Methanolic Solutions

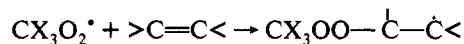
compound	$k, \text{L mol}^{-1} \text{s}^{-1}$			
	$\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$	$\text{CCl}_3\text{O}_2^\bullet$ ^a	$\text{CBr}_3\text{O}_2^\bullet$ ^a	$\sigma^{\bullet b}$
2-buten-1-ol	4.9×10^4	2.6×10^4	2.3×10^4	1.54
3-methyl-3-buten-1-ol	9.3×10^4	5.0×10^4	5.0×10^4	1.16
3-methyl-2-buten-1-ol	3.3×10^5	1.6×10^5	1.2×10^5	1.05
cyclohexene	2.1×10^5	9.5×10^4	9.1×10^4	0.78
2-methyl-2-butene	2.8×10^6	1.3×10^6		0.49
1-methyl-1-cyclohexene	3.2×10^6	1.3×10^6		0.29
2,3-dimethyl-2-butene	3.1×10^7	1.4×10^7	1.0×10^7	0.00
2-methyl-3-ethyl-2-pentene	9.7×10^6	3.2×10^6	2.5×10^6	-0.20
1,2-dimethylcyclohexene	8.0×10^6	3.4×10^6	3.3×10^6	-0.20
styrene	5.7×10^5	3.2×10^5	2.1×10^5	2.07

^a Reference 13, except for the results for 2-methyl-2-butene and 1-methyl-1-cyclohexene, which were measured in this study. ^b Taft σ^{\bullet} substituent constants calculated as the sum of the individual σ^{\bullet} values of the substituents on each double bond, taking $\text{H} = +0.49$; $\text{CH}_3 = 0.00$; $\text{C}_2\text{H}_5 = -0.10$; $\text{C}_6\text{H}_5 = +0.60$; $\text{CH}_2\text{OH} = +0.56$; $\text{CH}_2\text{CH}_2\text{OH} = +0.18$ (estimated from other values). For the cyclic alkenes we calculated the values by assuming two open ends.

The precursor carbon-centered radical for $\text{CCl}_3\text{O}_2^\bullet$ was formed from the reduction of CCl_4 ; for $\text{CF}_3\text{O}_2^\bullet$, the reduction of CF_3Br was employed; $\text{CF}_2\text{ClO}_2^\bullet$ arose from CF_2Cl_2 , $\text{CF}_2\text{BrO}_2^\bullet$ from CF_2Br_2 , $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$ from CF_3CCl_3 , $\text{CF}_3\text{CF}_2\text{O}_2^\bullet$ from $\text{CF}_3\text{CF}_2\text{I}$, and $(\text{CF}_3)_2\text{CFO}_2^\bullet$ from $(\text{CF}_3)_2\text{CFI}$. The perfluoroalkyl iodides were obtained from PCR, Inc., CF_3Br and CF_2Cl_2 were obtained from Matheson, CF_2Br_2 was from Aldrich, and CCl_4 was from Mallinckrodt. Chlorpromazine was from Sigma; Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid), *p*-methoxyphenol, and most alkenes were from Aldrich; 1,2-dimethylcyclohexene and 2,3-dimethyl-2-butene were from Chemical Samples.

Results and Discussion

Effect of Alkene Substituents on the Addition Reaction. The rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$ with 10 alkenes (Table 1) vary between 5×10^4 and $3 \times 10^7 \text{ L mol}^{-1} \text{s}^{-1}$. The variation in the rate constant with substituents about the double bond is consistent with addition as the main reaction path.



The same pattern was observed for the reactions of other

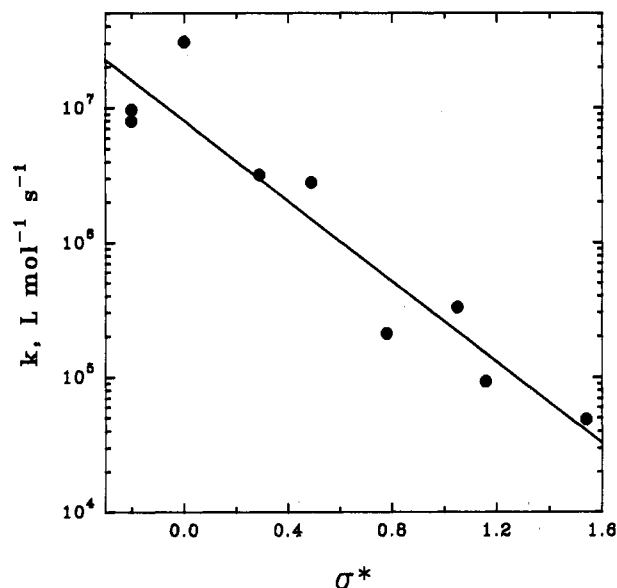


Figure 2. Correlation of the rate constants for the reaction of $\text{CF}_3\text{CCl}_2\text{O}_2^*$ with unsaturated compounds and the substituent constant σ^* .

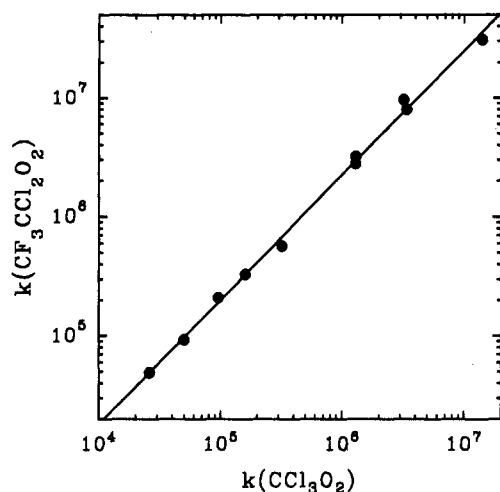


Figure 3. Correlation between the rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^*$ and CCl_3O_2^* with various alkenes.

halogenated peroxyl radicals.^{11,13} The results for CCl_3O_2^* and CBr_3O_2^* are included in Table 1 for comparison. The conclusion that the primary reaction is electrophilic addition is based on the good correlation observed between the logarithms of the rate constants and the Taft σ^* substituent constants. The values of σ^* , calculated as the sum of the individual values for the substituents on the double bond,¹⁹ are included in Table 1. The correlation for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^*$ with aliphatic alkenes (Figure 2) and earlier similar correlations^{11,13} show considerable scatter. (Styrene, where the substituent effect may also involve resonance stabilization, is not included in the correlation.) Much better correlations are found, however, among the rate constants for the various peroxyl radicals. Figure 3 shows the correlation between the rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^*$ with the corresponding reactions of CCl_3O_2^* ; a similar correlation is observed with CBr_3O_2^* . The scatter in the σ^* plots points to a general tendency for the reactions of the peroxyl radicals with the larger alkenes to be slower than expected. For example, the reactions of 2-methyl-3-ethyl-2-pentene and 1,2-dimethylcyclohexene are slower than the reaction of 2,3-dimethyl-2-butene, even though they have an equal degree of substitution and their σ^* values are more negative. These results indicate that there is a steric effect in the reactions of the larger alkenes with peroxyl radicals.

TABLE 2: Rate Constants for Reactions of (Haloalkyl)peroxyl Radicals with Alkenes^a in Methanolic Solutions

radical	$k, \text{L mol}^{-1} \text{s}^{-1}$				
	CH	MB	MCH	DMB	DMCH
CBr_3O_2^*	9.1×10^4 ^b			1.0×10^7 ^b	3.3×10^6 ^b
CCl_3O_2^*	9.5×10^4 ^b	1.3×10^6	1.3×10^6	1.4×10^7 ^b	3.4×10^6 ^b
CF_3O_2^*	7.5×10^5 ^b	1.8×10^7	1.7×10^7	2.2×10^8 ^b	7.5×10^7 ^b
$\text{CF}_2\text{ClO}_2^*$	4.5×10^5	9.4×10^6	9.1×10^6	8.3×10^7	3.2×10^7
$\text{CF}_2\text{BrO}_2^*$	4.9×10^5	7.9×10^6	7.7×10^6	7.7×10^7	2.7×10^7
$\text{CF}_3\text{CCl}_2\text{O}_2^*$	2.1×10^5	2.8×10^6	3.2×10^6	3.1×10^7	8.0×10^6
$\text{CF}_3\text{CF}_2\text{O}_2^*$	1.7×10^6	1.9×10^7	2.6×10^7	1.3×10^8	6.7×10^7
$(\text{CF}_3)_2\text{CFO}_2^*$	7.7×10^5	6.8×10^6	6.4×10^6	5.0×10^7	2.5×10^7
$-\text{O}_2\text{CCCl}_2\text{O}_2^*$				$<1 \times 10^5$ ^c	

^a CH, cyclohexene; MB, 2-methyl-2-butene; MCH, 1-methylcyclohexene; DMB, 2,3-dimethyl-2-butene; DMCH, 1,2-dimethylcyclohexene.

^b Reference 13. ^c Addition of 124 mmol L^{-1} DMB to a solution containing 4.8 mmol L^{-1} chlorpromazine resulted in no measurable change in the rate of formation of the CIPz radical, suggesting that the rate constant for the reaction of $-\text{O}_2\text{CCCl}_2\text{O}_2^*$ with DMB is less than $10^5 \text{L mol}^{-1} \text{s}^{-1}$.

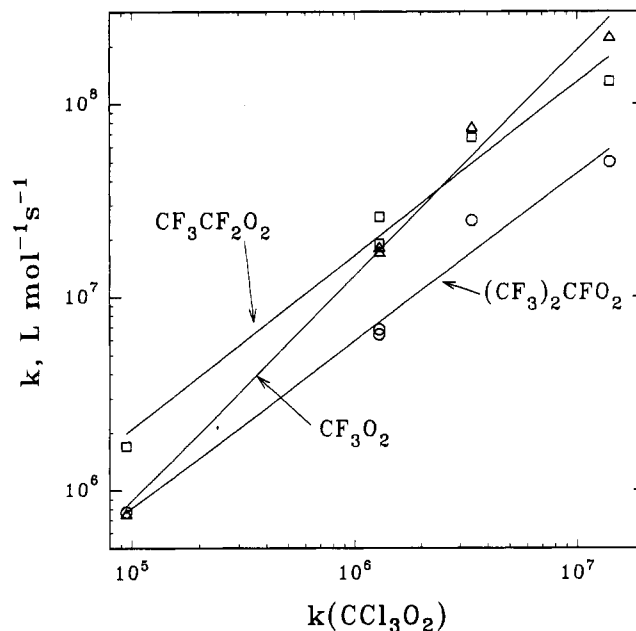


Figure 4. Correlation between the rate constants for the reactions of the perfluorinated peroxyl radicals with alkenes and the reactions of CCl_3O_2^* with the same alkenes.

Effect of Peroxyl Radical Substituents on the Addition Reaction.

The results for a number of different haloalkyl radicals reacting with five alkenes are presented in Table 2 (included, for comparison, are some results for CF_3O_2^* , CCl_3O_2^* , and CBr_3O_2^* from earlier work). It is clear that the (trifluoromethyl)peroxyl radical is more reactive than the (trichloromethyl)peroxyl radical, which is slightly more reactive than the (tribromomethyl)peroxyl radicals. Substitution of a single chlorine or bromine for a fluorine in CF_3O_2^* reduces the reactivity by a factor of 2. Substitution of two chlorine atoms for two fluorine atoms, as between $\text{CF}_3\text{CF}_2\text{O}_2^*$ and $\text{CF}_3\text{CCl}_2\text{O}_2^*$, leads to a reduction in reactivity of a factor of about 7. Substitution of a CF_3 group for a F atom does not have a clear effect: it doubles the rate constant for cyclohexene but appears to be slightly deactivating for 2,3-dimethyl-2-butene and for 1,1-dimethylcyclohexene. Substitution of two CF_3 groups leads to a result which appears even more anomalous: CF_3O_2^* and $(\text{CF}_3)_2\text{CFO}_2^*$ react with cyclohexene with equal rate constants; for the more substituted alkenes, CF_3O_2^* is the more reactive. This behavior is illustrated in Figure 4, where the rate constants for the three totally fluorinated peroxyl radicals are plotted against the rate constants for the reactions of CCl_3O_2^* . The lines for $\text{CF}_3\text{CF}_2\text{O}_2^*$ and $(\text{CF}_3)_2\text{CFO}_2^*$ are parallel, while the line for CF_3O_2^* increases more rapidly. These results seem to suggest an effect

TABLE 3: Rate Constants for Reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$ and $\text{CCl}_3\text{O}_2^\bullet$ Radicals with Organic Reductants in Methanolic Solutions

substrate	k , $\text{L mol}^{-1} \text{s}^{-1}$	
	$\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$	$\text{CCl}_3\text{O}_2^\bullet$
chlorpromazine	1.7×10^8	8.6×10^7
Trolox	4.2×10^7	3.1×10^7
<i>p</i> -methoxyphenol	7.5×10^5	4.9×10^5

TABLE 4: Rate Constants for Reactions of (Haloalkyl)peroxyl Radicals with Chlorpromazine in Methanolic Solutions

radical	k , $\text{L mol}^{-1} \text{s}^{-1}$	radical	k , $\text{L mol}^{-1} \text{s}^{-1}$
$\text{CCl}_3\text{O}_2^\bullet$	8.6×10^7	$\text{CF}_3\text{CF}_2\text{O}_2^\bullet$	3.6×10^8
$\text{CF}_2\text{ClO}_2^\bullet$	1.5×10^8	$(\text{CF}_3)_2\text{CFO}_2^\bullet$	3.0×10^8
$\text{CF}_2\text{BrO}_2^\bullet$	1.7×10^8	$-\text{O}_2\text{CCl}_2\text{O}_2^\bullet$	9.6×10^6
$\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$	1.7×10^8		

of steric hindrance, which reduces the rate constants for the reactions of $\text{CF}_3\text{CF}_2\text{O}_2^\bullet$ with the larger alkenes and the rate constants for the reactions of $(\text{CF}_3)_2\text{CFO}_2^\bullet$ with all the alkenes.

Effect of Substituents on the Electron-Transfer Reactions. We have also measured rate constants for the reactions of $\text{CCl}_3\text{O}_2^\bullet$ and $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$ with several reductants by following the buildup in absorbance after the pulse (chlorpromazine at 525 nm, Trolox and *p*-methoxyphenol at 420 nm). These results are presented in Table 3. In Table 4, we present results on the reaction of several haloperoxyl radicals with chlorpromazine. As for the reactions with the alkenes, oxidation of these reductants by $\text{CF}_3\text{CCl}_2\text{O}_2^\bullet$ takes place with rate constants about 1.6 ± 0.3 times higher than those for $\text{CCl}_3\text{O}_2^\bullet$. Thus, the replacement of a Cl by a CF_3 increases with reactivity of the radical. The same effect is also seen in Table 4 when comparing the results of $\text{CF}_2\text{ClO}_2^\bullet$ and $\text{CF}_3\text{CF}_2\text{O}_2^\bullet$.

Implications for Atmospheric Chemistry. The gas-phase rate constant for the reaction of $\text{CF}_3\text{O}_2^\bullet$ with NO is about $9 \times 10^9 \text{ L mol}^{-1} \text{s}^{-1}$; the reaction of $\text{CF}_3\text{O}_2^\bullet$ with NO_2 , at the high pressure limit, has a rate constant of about 4×10^9 .² In this work, we have found that the rate constants for the reactions of the halogenated peroxyl radicals with alkenes in methanol reach a maximum at about $2 \times 10^8 \text{ L mol}^{-1} \text{s}^{-1}$. We do not yet know the reactivity of halogenated peroxyl radicals toward alkenes in the *gas phase*. The reactions of $\text{CCl}_3\text{O}_2^\bullet$ with alkenes do show a variation in rate constant with solvent, but no particular correlation with solvent parameters was found.¹³ Rate constants for the reactions of some organic peroxyl radicals derived from alcohols with nitric oxide were found to be similar in water and alcoholic solvents to those measured in the gas phase.²⁰

The fact that the rate constants do not continue to increase with increasing fluorine substitution for the more reactive alkenes but, instead decrease suggests that the rate constants for the reactions of halogenated peroxyl radicals with terpenes or other atmospheric alkenes will be at this value or lower. Therefore, the concentration of alkenes in the atmosphere must be at least 20–50 times greater than that of the nitrogen oxides for the reaction rates to be of equal magnitude. The concentration of nitrogen

oxides is highly variable, with a global value of about 0.1–1 ppb. In urban areas, the concentration averages about 24 ppb.²¹ Alkene concentrations are also highly variable. Most measurements have been made in urban areas and range up to 20 ppb for individual branched-chain alkenes. (Ethene and propene have even higher concentrations; they are unlikely, however, to be reactive toward these peroxyl radicals.) In rural areas, the concentrations of these alkenes, with the exception of isoprene, are likely to be much lower. Terpenes, however, are emitted in large quantities by vegetation. Ambient concentrations of 0.1–1 ppb have been reported near forests.²¹ Together, these data suggest that the concentrations of the nitrogen oxides and of the reactive alkenes are likely to be similar within a given area, probably within a factor of 10. This would indicate that the halogenated peroxyl radicals are not likely to react with the alkenes, but will react with ambient NO and NO_2 .

Acknowledgment. This work was supported in part by the United States Army under MIPR # M-G-164-93. The authors thank Dr. A. W. Miziolek of the Army Research Laboratory, Aberdeen Proving Ground, for helpful discussions.

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