

## Kinetic Study of the OH Reaction with the Hydrofluoroethers C<sub>4</sub>F<sub>9</sub>-O-CH<sub>3</sub> and C<sub>4</sub>F<sub>9</sub>-O-C<sub>2</sub>H<sub>5</sub> by the Relative Rate Method

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The kinetics of the OH reactions with methoxy-nonafluorobutane and ethoxy-nonafluorobutane was studied by the relative rate method at 298 K and 1013 hPa using GC-MS and long path Fourier transform infrared detection. The average results, with 3σ statistical errors, are  $k_{\text{OH-C}_4\text{F}_9\text{OCH}_3} = 1.48(7) \times 10^{-14}$  and  $k_{\text{OH-C}_4\text{F}_9\text{OCH}_2\text{CH}_3} = 1.00(3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. © Anita Publications. All rights reserved.

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This work is dedicated to Prof. Thorvald Pedersen on his retirement from the Department of Chemistry, Copenhagen University. His continuous quest for scientific explanations to everyday phenomena has been an inspiration to us all.

### 1 Introduction

The CFCs and HCFCs have been important classes of chemical compounds in the industrial society for years. They are used in a variety of applications including refrigeration, cleaning of critical electronic and precision mechanical components, air conditioning, medical products, and energy-efficient insulation. Unfortunately, they are greenhouse gases – some of them have considerable global warming potentials – and are becoming ever more important relatively to the other greenhouse gases with lower growing rates (CO<sub>2</sub>, CH<sub>4</sub>). They are also able to destroy stratospheric ozone. The identification of suitable industrial alternatives to these compounds remains a challenge due to the complex combination of performance, safety and environmental properties required. Hydrofluoroethers, HFEs, have been suggested as substituents for CFCs and HCFCs in applications such as the cleaning of electronic components, refrigeration and carrier compounds for lubricants. Removal of HFEs from the troposphere will primarily be initiated by reaction with OH radicals since reaction with Cl, O<sub>3</sub> and NO<sub>3</sub> or photolysis is expected to be negligible. In order to ascertain the environmental impact of HFEs released into the troposphere, their atmospheric lifetimes with respect to reaction with OH radicals, and the nature and fate of the resulting oxidation products are required.

As part of ongoing work in our laboratory concerning the atmospheric chemistry of fluorinated alcohols and ethers we have studied the reactions of OH radicals with two new industrially used hydrofluoroethers C<sub>4</sub>F<sub>9</sub>-O-CH<sub>3</sub> (HFE-7100) and C<sub>4</sub>F<sub>9</sub>-O-C<sub>2</sub>H<sub>5</sub> (HFE-7200). The rate coefficients of the OH reaction with the two ethers have previously been reported by Wallington *et al.*<sup>1</sup> and by Christensen *et al.*,<sup>2</sup> respectively.

### 2 Experimental

The OH reaction rate coefficients were determined by the relative rate method



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where A is the reactant of interest, R is the reference compound, X is the radical, and  $k_I$  and  $k_{II}$  are the reaction rate coefficients. Assuming that the reactant and reference compounds are lost solely via reaction with the radical species of interest and that they are not reformed in any process, the relative rate coefficient,  $k_{rel}$ , can be obtained by the following relation:

$$\ln\left\{\frac{[A]_0}{[A]_t}\right\} = k_{rel} \cdot \ln\left\{\frac{[R]_0}{[R]_t}\right\} \quad k_{rel} = \frac{k_I}{k_{II}} \quad (1)$$

in which  $[A]_0$ ,  $[R]_0$ ,  $[A]_t$  and  $[R]_t$  denote the concentrations of A and R at time zero and  $t$ , respectively. A plot of  $\ln\{[A]_0/[A]_t\}$  vs.  $\ln\{[R]_0/[R]_t\}$  will give  $k_{rel}$  as the slope. Data from independent experiments were analysed jointly according to eqn. (1) using a weighted least squares procedure including uncertainties in both reactant concentrations and allowing a zero-point offset.<sup>3</sup>

The measurements were performed at  $1013 \pm 15$  hPa and  $298 \pm 2$  K in synthetic air in a 250 L smog chamber of electropolished stainless steel. *In situ* air analyses were obtained with an Agilent 6890/5973 GC-MS employing chemical ionisation (CI). The GC was operated under isothermal conditions at 40 °C. A constant overpressure of ca. 5 hPa was applied to the reactor to ensure a steady flow of ca. 20 mL/min through the 0.5 mL GC sampling loop. An inert tracer (perfluorodimethylcyclohexane) was added to monitor the dilution of the reactants. The compounds studied and employed as reference compounds all had unique mass peaks, which made it possible to operate the MS in the SIM mode. The relative concentrations of methoxy-nonafluorobutane, ethoxy-nonafluorobutane, acetonitrile, chloroform, and perfluorodimethylcyclohexane were determined from the  $m/z$  signals at: 231 ( $C_4F_8OCH_3^+ = C_4F_9OCH_3 + H^+ - HF$ ), 245 ( $C_4F_8OCH_2CH_3^+ = C_4F_9OCH_2CH_3 + H^+ - HF$ ), 41 ( $CH_4CN^+ = CH_3CN + H^+$ ), 83 ( $CHCl_3 + H^+ - HCl$ ), and 381 ( $(CF_3)_2C_6F_{10} + H^+ - HF$ ), respectively.

Hydroxyl radicals were generated by photolysis of ozone/ $H_2$  mixtures. Typical volume fractions of  $H_2$  and ozone were 10000 and 500 ppm, respectively. Ozone was produced from oxygen by using a TRI-OX Ozone Generator model T-200 that converts approximately 2 % of the oxygen gas flow to ozone. The photodissociation of ozone was accomplished by two Philips TUV 30W lamps ( $\lambda_{max} \sim 253.7$  nm) mounted in a quartz tube in the smog chamber; photolysis was done in time intervals of 1-5 minutes. Synthetic air ( $CO + NO_x < 100$  ppb,  $C_nH_m < 1$  ppm), ethane (99.0 %), and oxygen gas (99.95 %) were delivered from AGA. Methoxy-nonafluorobutane, ethoxy-nonafluorobutane, acetonitrile and chloroform were standard commercial chemicals with purity better than 98 %; the HFE's were industrial mixtures of the *n*- and *i*-nonafluorobutane isomers.

The volume fractions of the organic compounds were typically 2–3 ppm. The rate coefficient of the OH reaction with methoxy-nonafluorobutane was determined relatively to those of acetonitrile and chloroform, while the rate coefficients of the OH reactions with ethoxy-nonafluorobutane were determined relative to those of chloroform and methoxy-nonafluorobutane, respectively. The organic compounds did not undergo photolysis under our experimental conditions and they were chemically stable in the reaction chamber when the photolysis lamps were turned off.

### 3 Results

$C_4F_9-O-CH_3 + OH$ . The reaction was studied using  $CH_3CN$  and  $CHCl_3$  as reference compounds. The commercial sample of methoxy-nonafluorobutane (HFE-7100) is a ca. 50:50 mixture of the *n*- and *i*-isomers of nonafluorobutane. We were not able to separate the isomers in the capillary GC column at 40 °C. In addition, the fragmentation pattern observed in the CI-MS spectra of the two isomers were nearly identical, and we can therefore only present average data for the isomers. Figure 1 shows plots of  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  vs.  $\ln\{[CH_3CN]_0/[CH_3CN]_t\}$  and  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  vs.  $\ln\{[CHCl_3]_0/[CHCl_3]_t\}$  with slopes of  $0.663 \pm 0.009$  and  $0.151 \pm 0.004$ , respectively. The recommended OH reaction rate coefficients for acetonitrile and chloroform are  $2.2 \times 10^{-14}$  and  $1.0 \times 10^{-13}$  cm<sup>3</sup>

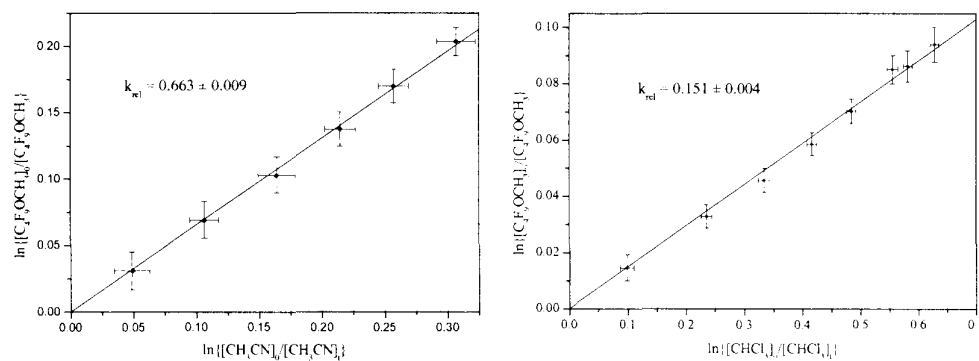


Figure 1. (A)  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  vs.  $\ln\{[CH_3CN]_0/[CH_3CN]_t\}$  during the reaction with OH radicals. (B)  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  vs.  $\ln\{[CHCl_3]_0/[CHCl_3]_t\}$  during the reaction with OH radicals.

molecule<sup>-1</sup> s<sup>-1</sup>,<sup>4</sup> respectively, which places the absolute rate coefficient of the OH + methoxy-nonafluorobutane reaction at  $1.46(6)$  and  $1.51(12) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, see Table 1.

$C_4F_9-O-C_2H_5 + OH$ . The reaction was studied using  $CHCl_3$  and methoxy-nonafluorobutane as reference compounds. The commercial sample of ethoxy-nonafluorobutane (HFE-7200) is a *ca.* 50:50 mixture of the *n*- and *i*-isomers of nonafluorobutane. As in the case of methoxy-nonafluorobutane, we could not separate the isomers in the capillary column at 40 °C, and the fragmentation pattern observed in the CI-MS spectra of the isomers were also nearly identical. Figure 2 shows plots of  $\ln\{[C_4F_9OCH_2CH_3]_0/[C_4F_9OCH_2CH_3]_t\}$  vs.  $\ln\{[CHCl_3]_0/[CHCl_3]_t\}$  and  $\ln\{[C_4F_9OCH_2CH_3]_0/[C_4F_9OCH_2CH_3]_t\}$  vs.  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  with slopes of  $1.088 \pm 0.022$  and  $6.53 \pm 0.13$ , respectively, which places the absolute rate coefficient of the OH + ethoxy-nonafluorobutane reaction at  $10.9(6)$  and  $9.70(20) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, see Table 1.

#### 4 Discussion

Table 1 gives a comparison of the results from the different studies of the OH reaction with the two fluorinated ethers. The reaction rate coefficients measured in this work approximately 25 % higher than

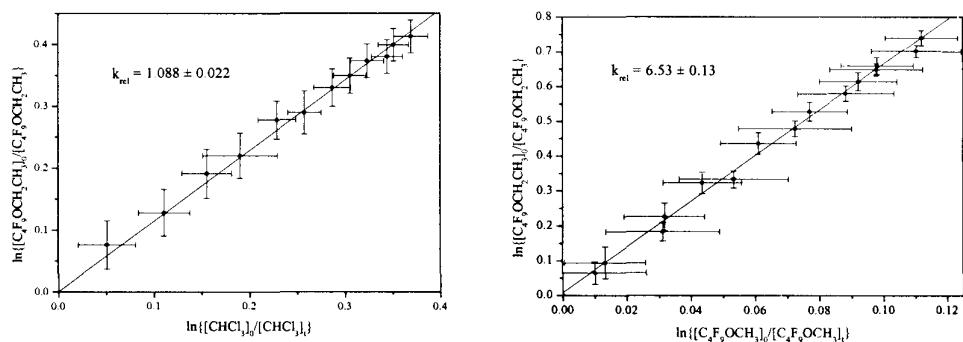


Figure 2. (A)  $\ln\{[C_4F_9OCH_2CH_3]_0/[C_4F_9OCH_2CH_3]_t\}$  vs.  $\ln\{[CHCl_3]_0/[CHCl_3]_t\}$  during the reaction with OH radicals. (B)  $\ln\{[C_4F_9OCH_2CH_3]_0/[C_4F_9OCH_2CH_3]_t\}$  vs.  $\ln\{[C_4F_9OCH_3]_0/[C_4F_9OCH_3]_t\}$  during the reaction with OH radicals.

Table 1. Comparison of measured rate coefficients for the OH reactions with methoxy-nonafluorobutane and ethoxy-nonafluorobutane.

OH + C <sub>4</sub> F <sub>9</sub> OCH <sub>3</sub>			OH + C <sub>4</sub> F <sub>9</sub> OCH <sub>2</sub> CH <sub>3</sub>		
$k_{\text{OH}}$ /10 <sup>-14</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Method <sup>a</sup>	Reference	$k_{\text{OH}}$ /10 <sup>-14</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Method <sup>a</sup>	Reference
1.46 ± 0.06 <sup>b</sup>	RR-GC/MS	This work	10.9 ± 0.6 <sup>c</sup>	RR-GC/MS	This work
1.51 ± 0.12 <sup>c</sup>	RR-GC/MS	This work	9.70 ± 0.20 <sup>e</sup>	RR-GC/MS	This work
1.2 <sup>d</sup>	RR-FTIR	Ref. 1	6.4 ± 0.7 <sup>d,f</sup>	RR-FTIR	Ref. 2
			7.7 ± 0.8 <sup>d,g</sup>	RR-FTIR	Ref. 2
			5.3 ± 1.1 <sup>f,h</sup>	RR-FTIR	Ref. 2

<sup>a</sup> RR = relative rate; FTIR = Fourier transform infrared spectroscopy; GC = gas chromatography, MS = mass spectrometry. <sup>b</sup> Relative to acetonitrile,  $k = 2.2 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; the uncertainties quoted in this study represent the 3 $\sigma$  statistical error only. <sup>c</sup> Relative to chloroform,  $k = 1.0 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>d</sup> Relative to methylchloride,  $k = 3.6 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>e</sup> Relative to C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>,  $k = 1.5 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>f</sup> Results for the *n*-isomer, <sup>g</sup> Results for the *i*-isomer. <sup>h</sup> Relative to methane,  $k = 6.3 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

the previously reported values.<sup>1,2</sup> We believe that main the reason to this lies in the small reactor and the rather high organic reactant concentrations used in the previous studies.

The atmospheric lifetimes of the HFE's may be estimated by neglecting the temperature dependence of the OH-reaction, and assuming a homogenous distribution and an average daily and global OH concentration of 1×10<sup>6</sup> molecules cm<sup>-3</sup>. The lifetimes of HFE-7100 and HFE-7200 may then be estimated as ca. 2 years and 4 months, respectively. Alternatively, one may assume a global distribution and a temperature dependency of the OH-reactions similar to that of CH<sub>3</sub>CCl<sub>3</sub>, which has an atmospheric OH-lifetime of 6.3 years.<sup>5</sup> In this approximation, the estimated atmospheric lifetimes are ca. 4 years and 7 months, respectively. In any case, the atmospheric lifetimes of HFE-7100 and HFE-7200 are sufficiently short such that their global warming potentials are much smaller than those of the CFCs and PFCs to be phased out: GWP<sub>100 year</sub>(HFE-7100) = 0.091,<sup>1</sup> and GWP<sub>100 year</sub>(HFE-7200) = 0.014.<sup>2</sup>

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