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Laser Magnetic Resonance Study of Reactions of OH Radicals with Some Halogenated Hydrocarbons

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The recent discovery of halogenated hydrocarbon molecules in the atmosphere [1] and the suggestion of a possible destructive effect of atomic chlorine on the stratospheric ozone [2] have initiated a great deal of study and concern about the atmospheric chemistry of halogenated hydrocarbons. One process which may provide an important atmospheric sink for these molecules is their reaction with OH radicals.

We have studied the OH reactions of a number of chloro-fluoromethane, ethane, and ethylene compounds at room temperature using laser magnetic resonance detection of OH [3]. Some preliminary results of these measurements are given in the table below. The reactions with ethylene species are observed in the transition from termolecular to bimolecular kinetics in the pressure range 0.5 to 10 Torr helium.

Support from the NBS Office of Air and Water Measurement is gratefully acknowledged.

1 J. E. Lovelock, Nature, 252 (1974) 292 and references cited therein.
2 M. J. Molina and F. S. Rowland, Nature, 249 (1974) 810
3 C. J. Howard and K. M. Evenson, J. Chem. Phys., 61 (1974) 1943.

Preliminary Rate Constants For Some OH Reactions

Reaction	T = 296 °K Rate Constant (cm^3/molecules)
Methane Compounds	
$OH + CH_4 \rightarrow CH_3 + H_2O$	9.5×10^{-15}
$OH + CH_3F \rightarrow CH_2F + H_2O$	16
$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	36
$OH + CH_2F_2 \rightarrow CHF_2 + H_2O$	7.8
$OH + CHF_3 \rightarrow CF_3 + H_2O$	0.2
$OH + CHF_2Cl \rightarrow CFCl_2 + H_2O$	3.4
$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	26
$OH + CF_4 \rightarrow$	<0.4
$OH + CF_3Cl \rightarrow$	<0.7
$OH + CF_2Cl_2 \rightarrow$	<0.4
$OH + CFCl_3 \rightarrow$	<0.5
Ethane Compounds	
$OH + CH_3CH_3 \rightarrow CH_3CH_2 + H_2O$	290×10^{-15}
$OH + CH_3CH_2Cl \rightarrow CH_3CHCl + H_2O$	390
$OH + CF_2HCH_3 \rightarrow CF_2HCH_2 + H_2O$	33
$OH + CF_2ClCH_3 \rightarrow CF_2ClCH_2 + H_2O$	7.3
Ethylene Compounds	
$OH + CH_2CH_2 + He \rightarrow CH_2CH_2OH + He$	$k_\infty = 2.5 \times 10^{-12}$
$OH + CH_2CHCl + He \rightarrow CH_2CHClOH + He$	5.8
$OH + CF_2CH_2 + He \rightarrow CF_2CH_2OH + He$	2.1
$OH + CClFCF_2 + He \rightarrow CClFCF_2OH + He$	5.4