Rate constants for the reactions of OH with ethane and some halogen substituted ethanes at 296 K

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(Received 26 January 1976)

Absolute rate constants for the reactions of OH radicals with C_2H_6 and twelve fluorine, chlorine, and bromine substituted ethane compounds are reported. The measurements are made at 296 K and pressures ranging from 100 to 1000 Pa (0.7–7 torr) using a discharge-flow system and laser magnetic resonance detection of OH. The results are similar to those of an earlier work on a series of methane compounds and indicate that the reaction mechanism is the abstraction of an H atom. Thus, completely halogenated molecules are relatively inert. The hydrogen containing molecules react with rate constants ranging from about 3 to 400×10^{-15} cm^3 molecule$^{-1} \cdot$sec^{-1}.

INTRODUCTION

The current controversy over the role of halogenated hydrocarbons in conveying chlorine and bromine to the stratosphere, where these atomic species are photolytically released to catalytically destroy ozone, is well documented.[1-4] A number of mechanisms have been proposed to compete with stratospheric photolysis as halocarbon sinks, including ion–molecule reactions, $O(^1D)$ atom reactions, heterogeneous processes, and OH radical reactions. Of these, only heterogeneous processes, which are very difficult to assess, and OH reactions remain viable. Our measurements of the reactivity of OH radicals for a series of single carbon molecules containing hydrogen, fluorine, chlorine, and bromine were reported earlier.[5] That work is in excellent agreement with other studies by Atkinson, Pitts and co-workers,[6] and Davis et al.,[7] which include important measurements of the temperature dependencies.

CH_3CCl_3 (methyl chloroform or 1,1,1-trichloroethane) is used extensively as a cleaning solvent, and it is estimated that in 1974 more than 330 million kilograms of CH_3CCl_3 were released into the atmosphere.[8] It has been detected in the northern troposphere at a mixing ratio of about 10^{-10}.[9] CH_2BrCH_2Br (ethylene dibromide or 1,2-dibromoethane) is also produced in large quantities. Much of this is used as an automobile fuel additive to aid in the volatilization of lead combustion products and is not likely to escape unreacted into the atmosphere. A smaller amount is used as a wood fumigant. CH_3CHF_2 (fluorocarbon 152a or 1,1-difluoroethane) is marketed and used in an azeotropic mixture with CF_2Cl_2 as a refrigerant. CH_3CClF_2 (fluorocarbon 142b or 1,1-difluoro-1-chloroethane) is used in a mixture with CF_2Cl_2 and $CFCl_3$ to produce an aerosol propellant. $CF_2ClCFCl_2$ (fluorocarbon 113, or 1,1,2-trifluorotrichloroethane) and CF_2ClCF_2Cl (fluorocarbon 114 or 1,2-dichlorotetrafluoroethane) and mixtures containing these compounds are probably released to the atmosphere in their applications as refrigerants, propellants, and blowing agents for rigid and resilient polymeric foams. In addition, other ethane type compounds containing hydrogen are being considered as replacements for CF_2Cl_2 and $CFCl_3$.

Thus there is a need for measurements of the reactions of OH radicals with ethane halocarbons. The present work covers some reactions of OH with ethane type molecules containing hydrogen, fluorine, chlorine, and bromine.

EXPERIMENTAL

The apparatus and rate constant measurement techniques are described in detail in previous work.[5,10] Briefly, the apparatus is a conventional discharge-flow system in which OH radicals are generated in a helium carrier gas stream by the fast reaction of H with NO_2. Typical concentrations are about $10^9 - 10^{11}$ molecules/cm^3 for OH, $8 \times 10^{12} - 6 \times 10^{15}$ molecules/cm^3 for reactant molecules, and $2.6 \times 10^{16} - 2.6 \times 10^{17}$ molecules/cm^3 for the helium carrier gas. The gas temperature is 296 K. Hydroxyl radicals are detected with a laser magnetic resonance spectrometer. A cw D_2O laser operating at a wavelength of 84.3 μm monitors relative OH concentrations by means of Zeeman modulated resonance absorption. The $OH(X^2\Pi_{3/2}, v=0, J=\frac{5}{2} - J=\frac{3}{2})$ magnetic component at 1.12 T (11.2 kG) is used primarily.

Reactant gas purity is a critical problem in many of these measurements, as noted earlier.[5] In particular, small quantities of volatile and highly reactive ($k \approx 5 \times 10^{-12}$ cm^3/molecule · s)[11] olefinic materials can cause serious errors when present in some of the relatively inert aliphatic halocarbons studied here. CH_3CCl_3 is a case worth noting. A special analyzed sample of CH_3CCl_3, which contained no chemical inhibitor, was obtained from the manufacturer. The major impurity in this sample, 0.39% CH_2CCl_2, is more volatile (bp 31.7 °C) than CH_3CCl_3 (bp 74.1 °C). Our first measurements yielded a rate constant of about 1.3×10^{-13} cm^3/molecule · s, which seemed large when compared to our other measurements on similar compounds. Therefore, we carried out a fractional distillation on a part of the sample, with the result that the observed rate coefficient was reduced considerably. With improved distillation technique, we eventually obtained a rate constant that could not be reduced by further purification steps. This sample was also analyzed and
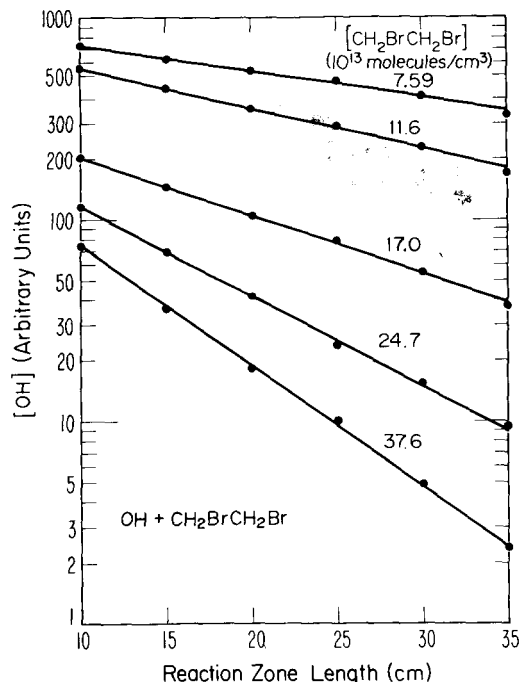
FIG. 1. Typical data for five measurements of the OH
+ CH$_2$BrCH$_2$Br reaction rate constant. The OH concentration is
shown as a function of the length of the reaction zone (equiva-
lent to reactant inlet position). The reactant gas concentration
is given for each measurement on the right side of the figure.
The average flow velocity $\bar{v}$ is 684 cm/sec and [He] = 1.36
×10^{17} atoms/cm^3.

found to be relatively free of CH$_2$CCl$_2$ (reduced by about
a factor of 30), although a higher concentration of high
boiling impurities remained.

The reactant gas materials have the following purity
levels: CH$_3$CH$_3$ > 99%, CH$_3$CH$_2$Cl > 99.7%, CH$_2$ClCH$_2$Cl
> 99.99% (analyzed), CH$_2$BrCH$_2$Br > 99.6% (analyzed),
CH$_3$CHF$_2$ > 99.9% (analyzed), CH$_3$CHCl$_2$ > 99.86% (anal-
yzed), CH$_3$CF$_2$Cl > 99.99% (analyzed), CH$_3$CCl$_3$ > 99.88%
(analyzed), CH$_2$ClCF$_3$ > 99.99% (analyzed), CHFClCF$_3$
> 99.8% (analyzed), CHCl$_2$CF$_3$ > 99.9% (analyzed),
CF$_2$ClCF$_2$Cl > 99.8% (analyzed), and CF$_2$ClCFCl$_2$
> 99.8% (analyzed). An analysis of the reactant mate-
rial used was obtained for those indicated to have been
analyzed. In all cases, the analysis was provided by
the manufacturers and was guided by their knowledge of
what important impurities result from the manufacturing
process. We are confident that the analyses show that
there are no significant impurities in the reactant
chemicals that would seriously affect the results. For
example, the impurities in CF$_2$ClCF$_2$Cl and CF$_2$ClCFCl$_2$
are almost entirely inert perhalogenated methane and
ethane compounds.

RESULTS AND DISCUSSION

Figure 1 shows a series of typical OH decay plots ob-
tained for the OH reaction with CH$_2$BrCH$_2$Br. The con-
centration of the reactant gas, [CH$_2$BrCH$_2$Br], is shown
on the right side of the figure for each set of points and
has been varied over a range of about a factor of 5 in
this series of experiments. The effective bimolecular

rate coefficient for each line can be obtained by dividing
the first-order rate constant from the slope of the line
by the average linear flow velocity $\bar{v}$ and the reactant
gas concentration. An alternative way to treat the data
is shown in Fig. 2, where the first-order rate constants
from Fig. 1 (in s^{-1}) are plotted as a function of the re-
actant concentration. An average bimolecular rate coef-
ficient for the whole set is given by the slope of the line
through the data. Since the line very nearly goes
through the origin, it is clear that the same result is
obtained by either averaging the individual bimolecular
rate coefficients or using the set of first-order con-
stants and concentrations as in Fig. 2. This is true of
nearly all of the reactions reported here.

After all of the measurements had been completed
using the usual boric acid coated flow tube, [10] we decided
to remeasure the rate constant for CH$_3$CHF$_2$ using a new
analyzed sample of reactant gas. In the meantime the
wall coating had been changed to phosphoric acid. The
results with this coating were quite different from the
previous boric acid coating set. The bimolecular rate
coefficient was found to decrease from about 4.8 to
about 3.4×10^{-14} cm^3/molecule · s with increasing reac-
tant concentration. The boric acid coating data show
no such effect. When the phosphoric acid coating set is
plotted, first-order rate constant vs reactant concen-
tration, as shown in Fig. 3, the problem is obvious.
As CH$_3$CHF$_2$ reactant is added to the flow tube, it
causes a small increase in the rate of destruction of OH
on the flow tube wall. Thus, each first-order rate con-
stant measurement, k' in Fig. 3, consists of two com-
ponents, a homogeneous (gas) reaction and a heteroge-
neous (wall) reaction. Fortunately, only the gas reac-
tion shows a dependence on reactant concentration, in-
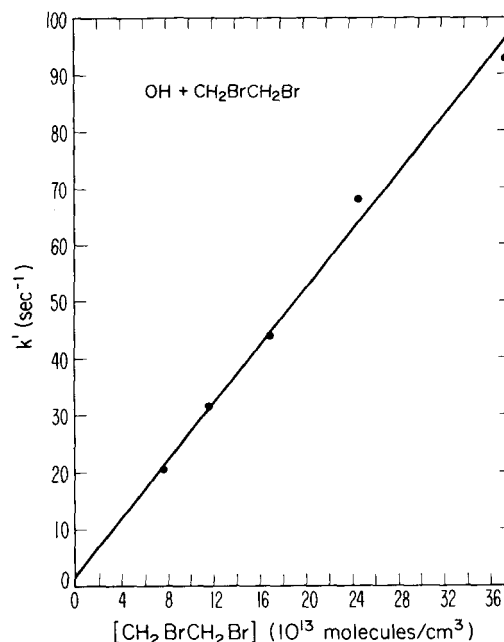dicating the wall is saturated with CH$_3$CHF$_2$ at the low-

FIG. 2. Plot of first order rate constants from data in Fig. 1
vs reactant gas concentration. The slope is the bimolecular
rate constant for this series for measurements of OH
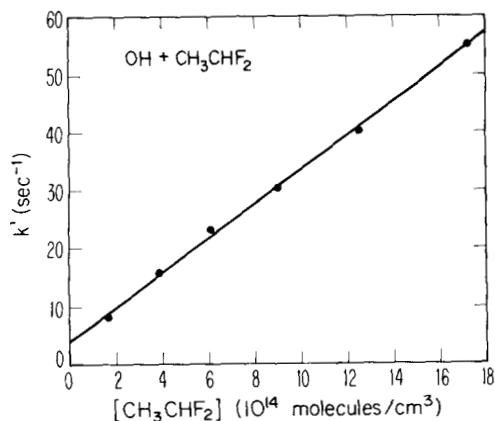+ CH$_2$BrCH$_2$Br.

FIG. 3. Plot of first order rate constants vs reactant gas concentration for six measurements of the OH + CH_3CHF_2 reaction using a phosphoric acid coated flow tube. The intercept is the change in the OH wall loss rate due to the addition of reactant gas. The slope is the bimolecular rate constant. $\bar{v} = 487$ cm/sec and $[He] = 5.84 \times 10^{16}$ atoms/cm^3.

est concentration used in this work. The resultant bimolecular rate coefficient, the slope, is in excellent agreement with the value measured with a boric acid wall coating.

The first-order OH wall loss rate constant for either boric acid or phosphoric acid coatings is about the same, about 20 s^{-1} in the absence of reactant gas. The phenomenon observed here is similar to that reported by Margitan et al.[12] recently for measurements on the (OH + HNO_3) reaction in a phosphoric acid coated reactor. In that study, the intercept with HNO_3 reactant was an order of magnitude larger than found here for CH_3CHF_2. At least for studies involving CH_3CHF_2, boric acid is a superior wall coating.

The rate constant measurements of this work are summarized in Table I with the results of others for comparison. The table also shows the number of measurements for each reactant, the average rate constant derived from these measurements, the standard deviation in parentheses, and the estimated total error.

Very few absolute rate constant measurements have been reported by others for OH reactions with ethane type molecules near room temperature. A few high temperature relative measurements have been reported and have been reviewed by Wilson[13] but will not be discussed here. The values given in Table I for other authors have been calculated for $T = 296$ K using their Arrhenius parameters.

Greiner[14] has studied the reactions of OH with a variety of alkanes, over the temperature range 300–500 K, using a flash photolysis–kinetic spectroscopy technique. His measurement for ethane, which includes a small correction (~10%) for secondary reaction, is in perfect agreement with the present work.

Cox et al.[15] have made measurements of the OH reactions of several halocarbons, including CH_3CF_2Cl and CH_3CCl_3. They use the photolysis of HNO_2 as a source of OH and a competitive reaction technique to derive rate constants relative to the (OH + CH_4) reaction. By

adopting a value of 7×10^{-15} cm^3/molecule · s for the (OH + CH_4) rate constant, the quantitative results shown in Table I are obtained. Their rate constant for CH_3CF_2Cl is close to our value but for CH_3CCl_3 is different by nearly a factor of 2, which is their estimate of their accuracy.

Davis et al.[7] have also measured rate constants for the OH reactions of CH_3CF_2Cl and CH_3CCl_3. They report the temperature dependence for the reactions from measurements using flash photolytic formation and resonance fluorescence detection of OH. Both results provide excellent agreement, with less than 10% difference from ours. This agreement is particularly gratifying in view of the complete difference in the measurement techniques used in the different studies.

As with the earlier methane compound measurements, we observe several trends in the OH reactivity of the ethane molecules with halogen atom substitution. Bromine and chlorine substitution are roughly equivalent and both tend to weaken the remaining (C–H) bonds and increase the OH reactivity.

Since we do not detect the reaction products, we cannot say with absolute certainty that the reaction mechanism is only hydrogen atom abstraction. However, all evidence clearly indicates that is the case.

There is not sufficient bond energy data for ethane type molecules to allow quantitative correlations with reactivity, but from our earlier correlation,[5] we can estimate the (C–H) bond energies for several of the compounds using their OH rate coefficients. Thus, we estimate D_{298}^0(C–H) = 104 kcal/mol for CH_3CF_2Cl, 101 kcal/mol for CH_3CCl_3, 101.5 kcal/mol for CH_2ClCF_3, 100.5 kcal/mol for $CHClFCF_3$, and 98.5 kcal/mol for $CHCl_2CF_3$. The accuracy of these estimates is probably about ± 2 kcal/mol.

TABLE I. Rate constant summary for this work and other measurements near 296 K.

Reactant	Number of measurements	Average (s. d.) ± error (10^{-15} cm^3/molecule · s)	Reference
CH_3CH_3	9	290(29) ± 60 290 ± 100	This work Greiner[14]
CH_3CH_2Cl	9	390(36) ± 70	This work
CH_2ClCH_2Cl	16	220(26) ± 50	This work
CH_2BrCH_2Br	19	250(18) ± 55	This work
CH_3CHF_2	20	31(2.3) ± 7	This work
CH_3CHCl_2	20	260(26) ± 60	This work
CH_3CF_2Cl	9	2.83(0.08) ± 0.42 4 3.09	This work Cox et al.[15] Davis et al.[7]
CH_3CCl_3	15	15(0.7) ± 3 28 15.3	This work Cox et al.[15] Davis et al.[7]
CH_2ClCF_3	12	10.5 (1.3) ± 2.3	This work
$CHClFCF_3$	16	12.4(0.6) ± 1.9	This work
$CHCl_2CF_3$	16	28.4(1.5) ± 4.3	This work
CF_2ClCF_2Cl	5	< 0.5	This work
CCl_2FCF_2Cl	3	< 0.3	This work

With the rate constant measurements reported here, it is possible to estimate the atmospheric lifetimes of the ethane type molecules with respect to OH radicals. The ideal way to compute this lifetime is with an extensive model of atmospheric chemistry which includes transport and temperature effects and natural atmospheric OH concentrations. A very crude estimate of the tropospheric life time τ can be made directly from a rate constant k in Table I and a typical average tropospheric concentration,[3] $[OH] = 10^6$ molecules/cm^3.

$$\tau = 1/k[OH] \ .$$

This predicts lifetimes ranging from about 2.6×10^6s (1 month) for CH_3CH_2Cl to about 3.5×10^8 s (10 yr) for CH_3CF_2Cl. Since transport into the stratosphere is a relatively slow process, these lifetimes suggest that a very small fraction of the CH_3CH_2Cl released in the troposphere will reach the stratosphere but a considerably larger fraction of CH_3CF_2Cl will survive long enough to reach the stratosphere. Authentic model calculations will allow the effect of these compounds on stratospheric ozone to be assessed.

Note added in proof: R. P. Overend, G. Paraskevopoulos, and R. J. Cvetanović, Can. J. Chem. **53**, 3374 (1975) have reported an additional measurement of the rate constant for the OH reaction with C_2H_6, $k = 2.64 \times 10^{-13}$ cm^3/molecule·s. This result is also in excellent agreement with the value reported here.

ACKNOWLEDGMENTS

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