Experimental and Estimated Rate. Constants

Reactions of 1 lydroxyl Radicals with Several Halocarbons

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long Abstract

Many halocarbons containing at least one hydrogen atom are currently of interest as possible chlorofluorocarbon replacements for refrigerants, lubricants, solvents, fire suppressants, and other applications. The tropospheric lifetime of these compounds, which is an important measure of their potential environmental impact, is determined primarily by their rate of reaction with the OH radical. Owing to the large number of possible isomeric compounds of these types, laboratory measurement of every one is very time-consuming. It is therefore desirable to use empirical methods to extrapolate the data whenever possible. In the present work a combination of experimental and estimated rate constants are presented for all possible F, Cl, and Br compounds of methane which contain at least one H atom, and also for a set of 25 compounds of ethane. Methods are shown which permit ext ension of the results to related compounds.

Methods

Relative Rate Measurements. 'J'he technique used in this work has been described in several recent publications.[1-6] The method involves measurement of the fractional loss of the reactant compound, compared to a reference compound, in the presence of OH. The OH radicals are produced by 254 nm photolysis of 03 (5-1 O x 10^{16} cm^{-3}) in the presence of water vapor (3-5 x 10^{17} cm^{-3}) or by direct photolysis of $11_2 0$ at 185 nm. The experiments are done in a temperature-controlled cylindrical quartz cell, operated either in a slow-flow or stopped-flow mode. The cylindrical cell is 10 cm in length and S cm in diameter, and is either water-jacketed (for the 0_3 photolysis experiments) or wrapped with heating tape and insulating material for the H_2O photolysis experiments. Residence times in the cell for the slow-flow mode are about one minute. Concentrations are monitored with a Nicolet 20SX FTIR, operated at 0.5 cm^{-1} resolution in the absorbance mode using a White cell with a three-meter path length. Other details of the experimental procedure are described in the papers referenced above.

Rate Constant Estimation Method. A simple group additivity approach has been used for the estimation of OH abstraction rate constants. It is similar in principle to the method described by Atkinson,[7] but somewhat different in detail. The total rate constant is obtained as the sum of the contributions from each C-H bond present in the molecule.

The logarithm (base 10) of the rate constant (per 1 l-atom) is given by the following equation :

$$\log k = \log k(CH_4) + G_1 \cdots G_3 \qquad (I)$$

The quantity log k, the logarithm of the CI 14 rate constant per I]-atom, is equal to -14.79, The G terms are the contributions for the various groups, such as Cl, Br, CH_3, CF_3, etc., which may be present on the carbon atom. In CH_3CF_3, for example, there is only one group, CF_3. The group contributions are determined by an optimization procedure such as that in the Excel spreadsheet program. In this procedure the cumulative difference between log k(experimental) and log k(estimated) is minimized by varying the group contributions to obtain the best overall fit, Significant parametrization is necessary to account for interactions between groups when more than onc group is present on the carbon atom. In the fitting procedure the maximum allowed error factor between estimated and experimental rate constants was set at 1.35. When more than one reactive site is present, the total rate constant is calculated as the sum of the separate contributions. This calculation can be expected to give a good estimate of the relative rates of attack at different sites in the molecule.

The range of group contributions can be extended by taking thcm as equal to those of similar groups. For example, the group contribution for C_2F_5 is taken to be identical to that of CF_3. The estimated rate constants are usually reliable to within a factor of 1.3 to 1.5. For the most part the accuracy is comparable to that of absolute rate constant measurements, which often are high due to impurity effects. When combined with estimated A-factors, the temperature dependence of the rate constants can be deduced. Thus an estimate of the entire Arrhenius expression can be obtained quickly and reliably.

The estimated A-factors are based on the previously reported observation[6] that ratios of A-factors as determined in relative rate experiments are very closely proportional to the number of H-atoms in the molecule (i. e., for reactive sites within the molecule where the I l-atoms arc equivalent). The value A/n= 8.011-13 cm3/molec.-s, where n is the number of II-atoms, is found to adequately represent the bulk of the reliable experimental data for 01 I abstraction reactions.

The compound CF3C112CI IF_2 (l IFC-245fa), with two different reactive sites, can be used as an example of the rate constant estimation method, using the fitted parameters. (Units arc cm^3/molec-s.).

$-CH_2-$ site: $\log k = -14.79 + G(CF_3) + G(CHF_2) + \log 2 = -15.07$
$k = 8.5E\text{-}16$

$-CHF_2$ site: $\log k = -14.79 + G(2F) + 0.37\ G(CH_2F) = -14.28$
$k = 5.2E\text{-}1S$

The quantity 0.37, determined in the fitting procedure, corrects for third group interactions. The sum of the rate constants for the two reactive sites is 6. 1E- 15, which compares well with the experimental values of 6.8E-15[8] and 7.211-159. in this example it

may be noted that CH_2F was used as a surrogate for the CF_3CH_2 group. The calculation predicts that the CHF_2 group is the major reaction site in the molecule, despite the fact that there is only one H atom at that site. This is a consequence of the strongly deactivating effect of the CF_3 group adjacent to the CH_2 site.

Results for the group contributions in the rate constant estimation method will be presented, as well as the experimental and estimated rate constant measurements for several HFCs and HCFCs.

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Table 1. Measured and Estimated Rate Constants for Halomethanes.

Compound	A-Factor	E/n	k(298 K)	Source
CHX_3				
CHF_3 (23)	6.4E-13	2354	2.4E-16	Hsu & DeMore[5]
CHF_2Cl (22)	7.1E-13	1478	5.0E-15	Hsu & DeMore[5]
CHF_2Br (22B1)	9.6E-13	1360	1.0E-14	Hsu & DeMore[5]
$CHCl_2F$ (21)	1.2E-12	1100	3.0E-14	JPL 94-26
CHBrClF (21B1)	8.0E-13	794	5.6E-14	estimate
$CHBr_2F$ (21B2)	8.0E-13	679	8.2E-14	estimate
$CHCl_3$ (20)	1.213-12	780	8.8E-14	Hsu & DeMore[4]
$CHCl_2Br$ (20B1)	8.0E-13	631	9.6E-14	estimate
$CHBr_2Cl$ (20B2)	8.0E-13	571	1.2E-13	estimate
$CHBr_3$ (20B3)	1.6E-12	711	1.5E-13	This work
CH_2X_2				
CH_2F_2 (32)	1.8E-12	1552	9.9E-15	Hsu & DeMore[5]
CH2FC1(31)	1.813-12	1197	3.2E-14	This work
CH_2FBr (31B1)	1.6E-12	1093	4.1E-14	estimate
CH_2Cl_2 (30)	2.2E-12	981	8.213-14	Hsu & DeMore[4]
CH_2BrCl (30B1)	1.8E-12	906	8.8E-14	'l'his work
CH_2Br_2 (30112)	1.9E-12	836	1.1E-13	This work
CH3X				
CH3F (41)	4.413-12	1655	1.7E-14	This work*
CH_3Br (40B1)	4.4E-12	1507	2.8E-14	Hsu & DeMore[4]
CH_3Cl (40)	4.4E-12	1470	3.2E-14	Hsu & DeMore[4]

Table 2. Measured and Estimated Rate Constants for Some Haloethanes.

Compound	A-Factor	E/R	k(298 K)	Source
CX_3CH_3				
CF_3CH_3 (143a)	1.2E-12	2055	1.2E-15	Hsu & DeMore[5]
CF_2ClCH_3 (142b)	1.3E-12	1800	3.111-15	JPL 94-26
CFC12Cl13(14 lb)	1.411-12	1630	5.9E-15	Huder & DeMore[3]
CCl_3CH_3 (1 40)	1.813-12	1550	9.913-15	JPL 94-26
CX_3CH_2F				
CF_3CH_2F (1 34a)	1.313-12	1740	3.8E-15	DeMore[2]
CF_2ClCH_2F (133b)	1.6E-12	1593	7.6E-15	estimate
$CFCl_2CH_2F$ (132c)	1.6E-12	1408	1.4E-14	estimate
CC13C112F (13 lb)	1.61? -12	1264	2.3E-14	estimate
CX_3CHF_2				
CF3C111;2 (125)	5.6E-13	1700	1.9E-15	JPL 94-26
CF_2ClCHF_2 (124a)	8. 0E-13	1657	3. 1E-15	estimate
$CFCl_2CHF_2$ (123b)	8. 0E-13	1588	3.913-15	estimate
CCl_3CHF_2 (122b)	8. 0E-13	1s34	4.7E-15	estimate
CX_3CHFCl				
CF_3CHFCl (1 24)	9.713-13	1459	7.3E-15	Hsu & DeMore[5]
$CF_2ClCHFCl$ (123a)	9.2E- 13	1281	1.2E-14	Orkin[16]
$CF_2BrCHFCl$ (123aB1)	9.3E-13	1252	1.413-14	This work
CC121X3117Cl (122a)	7.1E-13	1158	1.5E-14	Hsu & DeMore[5]
CCl_3CHFCl (121a)	8. 0E-13	1103	2.0E-14	estimate
CX_3CH_2Cl				
CF_3CH_2Cl (133a)	1.6E-12	1691	5.5E-15	estimate
CF_2ClCH_2Cl (132b)	1.6E-12	1476	1.1E-14	estimate
$CFCl_2CH_2Cl$ (131a)	1.6E-12	1291	2.1E-14	estimate
CCl_3CH_2Cl (130)	1.6E-12	1147	3.4E-14	estimate
CX_3CHCl_2				
CF_3CHCl_2 (1 23)	6.4E-13	910	3.013-14	Hsu & DeMore[5]
$CF_2ClCHCl_2$ (1 22)	8.31{-13	893	4.1E-14	This work
$CFCl_2CHCl_2$ (121)	8.013-13	827	5.0E-14	estimate
CCl_3CHCl_2 (120)	8.01?-13	774	6.011-14	estimate