



Rate constants and C–C bond scission ratios for hydrolysis of 2,2,3-trifluoro-3-(trifluoromethyl)oxirane determined by means of a closed-circulation reactor



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ABSTRACT

The hydrolysis rate constant of 2,2,2-trifluoro-3-(trifluoromethyl)oxirane (hexafluoropropene oxide; HFPO), a versatile precursor of fluorinated chemicals, was determined at 279–307 K, and the rate of hydrolysis was used to estimate the tropospheric lifetime of HFPO with respect to hydrolysis in clouds or uptake by the ocean. The low solubility of HFPO in water made it difficult to determine the hydrolysis rate constant because of mass-transfer limitation between the gas and liquid. A closed-circulation reactor was used to measure the rate of decrease of the partial pressure of HFPO while an HFPO-air mixture flowed over a stirred test solution under various experimental conditions. The rate of hydrolysis increased as the OH^- concentration increased in an aqueous NaOH solution but was almost independent of the H_2SO_4 concentration in aqueous H_2SO_4 solutions. Much scissioning of C–C bonds in HFPO produced carbon monoxide and trifluoroacetate in aqueous NaOH, but similar scissioning did not in water or aqueous H_2SO_4 . The first-order rate constant for the pH-independent hydrolysis (k_{water} in s^{-1}), the bimolecular rate constant for the hydroxide-catalyzed hydrolysis, and the temperature dependence of these parameters were estimated by simultaneously fitting equations based on a two-film model to the time series of HFPO partial pressures under different experimental conditions. The equations included the rate constants as common parameters. The product of k_{water} and the Henry's law constant, K_{H} (M Pa^{-1}), at a temperature of T (K) was determined to be $k_{\text{water}} \times K_{\text{H}} = 3.7 \times 10^{-11} \exp[-3300 \times (T^{-1} - 1/298.2)]$. The tropospheric lifetime of HFPO estimated using this equation indicates that removal of HFPO via hydrolysis in clouds is probably not a substantial sink of HFPO and suggests that, in the absence of other atmospheric sinks of HFPO, hydrolysis of HFPO in the ocean would be the major sink of HFPO.

1. Introduction

2,2,2-Trifluoro-3-(trifluoromethyl)oxirane (hexafluoropropene oxide; HFPO; $\text{CF}_3\text{CF}(\text{O})\text{CF}_2$) is a versatile precursor of fluorinated chemicals [1]. Its epoxide functional group has special features that allow it to play important roles in fluorinated chemical synthesis; HFPO has therefore been widely used in fluorochemical industrial processes. Much information about this use has accumulated, but little is known about the fate of HFPO after it is released into the environment. There is an absence of information about the physicochemical properties of HFPO, such as the rate constants for its gaseous reactions with OH radicals, which are relevant to processes involved in its removal from the atmosphere.

A potential mechanism for removing HFPO from the atmosphere is hydrolysis in cloud droplets or uptake by the ocean, because HFPO is known to hydrolyze in water at ambient temperature via Eq. (1) [2]:



The rate constant for this hydrolysis, k_{hyd} , must be known to estimate the atmospheric lifetime of HFPO with respect to hydrolysis in clouds or uptake by the ocean, but, to the author's knowledge, no values of k_{hyd} are available in peer-reviewed journals. The objective of this study was to determine k_{hyd} at ambient temperatures.

Hydrolysis of epoxides such as oxirane ($\text{CH}_2(\text{O})\text{CH}_2$) is a long-standing issue in the context of industrial applications and biological activities, and has been experimentally and theoretically investigated [3–12]. Furthermore, atmospheric hydrolysis of second-generation epoxides derived from isoprene has recently been studied with respect to environmental issues because these reactions can contribute to formation of secondary organic aerosols [13]. Experimental results suggest a rate expression that includes three kinetically distinguishable paths for the hydrolysis as follows [3,6]:

$$k_{\text{hyd}} = k_{\text{water}} + k_{\text{a}} [\text{H}_3\text{O}^+] + k_{\text{b}} [\text{OH}^-], \quad (2)$$

where k_{water} is the first-order rate constant for the pH-independent

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hydrolysis; k_a is the bimolecular rate constant for the acid-catalyzed hydrolysis; and k_b is the bimolecular rate constant for the hydroxide-catalyzed hydrolysis. For oxirane, values at 298 K have been reported to be $k_{\text{water}} = 5.7 \times 10^{-7} \text{ s}^{-1}$; $k_a = 9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$; and $k_b = 1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ [8]. The hydrolysis begins with the cleavage of a C–O bond of the epoxide ring. In the case of hydroxide-catalyzed and pH-independent paths, hydrolysis begins with a bimolecular nucleophilic substitution that involves the breaking of the epoxide C–O bond and formation of a covalent bond between the nucleophile and epoxide. The dominant hydrolytic products are diols such as glycols without C–C bond scissions for most epoxides.

For halogenated epoxides, hydrolysis of chlorinated ethene oxides such as trichloroethylene oxide [10,11] and tetrachloroethylene oxide [12] has been studied with particular emphasis on biological issues. The values of k_{water} and k_a for trichloroethylene oxide are more than 10^5 and 3 times, respectively, those for oxirane. The fact that carbon monoxide is the main hydrolytic product from trichloroethylene oxide and tetrachloroethylene oxide indicates that a C–C bond scission occurs after C–O bond cleavage of the epoxide ring during hydrolysis of these halogenated epoxides.

The relatively low solubility in water and absence of near-ultraviolet and visible absorption of HFPO may make it difficult to determine the value of k_{hyd} for HFPO. In this study, a reactor with a closed circulation system was used to observe decreases of the partial pressure of HFPO at various stirring speeds in test solutions with different pH values (e.g. deionized water and aqueous NaOH). The dependence of the rate of decrease of the partial pressure of HFPO on the stirring speed of the test solutions suggested that the rates of gaseous HFPO hydrolysis were limited by mass-transfer between the gas and liquid. A two-film model [14] was therefore used to determine values of k_{hyd} by fitting simultaneous equations, with k_{water} and k_b as common parameters, to the time series of HFPO partial pressures observed under different experimental conditions. Degradation products were found to differ between reactions in water and aqueous NaOH, and much C–C bond scissioning occurred in aqueous NaOH.

2. Results

2.1. Decreases of HFPO during the experimental runs at various stirring speeds of the test solutions with different pH values

Fig. 1 shows the residence ratio, P_t/P_0 , of HFPO on a logarithmic scale as a function of time for each experimental run in which an HFPO-air mixture flowed over deionized water at 295.9 K in the closed-circulation reactor. The parameter P_t is the partial pressure of HFPO at time t , and P_0 is the initial partial pressure of HFPO. In each experimental run, the deionized water was stirred at a prescribed rate that ranged from 0 to 1200 rpm. At 60 min, the circulation route was changed so that the gas mixture flowed over the deionized water. The resulting increase in the total volume corresponded to a 29% decrease in the partial pressure of HFPO and a corresponding abrupt decrease of the residence ratio at 60 min (Fig. 1).

When the HFPO-air mixture flowed over deionized water, the partial pressure of gaseous HFPO decreased with time. This observation, combined with the detection of degradation products such as F^- (described later), clearly indicated that hydrolysis of HFPO proceeded in the deionized water. The partial pressure of HFPO decreased with time according to first-order kinetics:

$$\ln(P_t/P_0) = -k_1 t, \quad (3)$$

where k_1 is the first-order rate constant for the rate of change of the partial pressure of gaseous HFPO.

That values of k_1 increased with increasing stirring speeds of the deionized water suggested that the rate of change of gaseous HFPO was limited by mass transfer of HFPO between the gas and liquid. The data

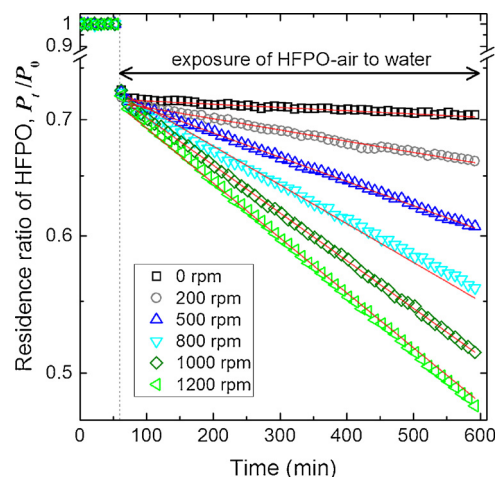


Fig. 1. Time course of the residence ratio of gas-phase HFPO (P_t/P_0) when the HFPO-air mixture was allowed to flow over deionized water stirred at rates ranging from 0 to 1200 rpm at a temperature of 295.9 K. The values of P_0 were 20.6, 20.8, 19.9, 20.6, 20.0, and 20.3 Pa for each experimental run in order of increasing stirring rates from 0 to 1200 rpm. Red lines indicate the values calculated from the fitting procedure (Section 2.2) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

in Fig. 1 alone could not be used to determine the value of k_{hyd} . A relationship such as Eq. (2) imposed further constraints on the value of k_{hyd} , as discussed later (Section 3.2). Therefore, similar experiments were performed for 10–50 mM aqueous NaOH solutions stirred at 800, 1000, and 1200 rpm at 295.9 K (Fig. 2, panels a, b, and d) and for 10–30 mM aqueous H_2SO_4 solutions stirred at 1000 rpm at 295.9 K (Fig. 2, panel c).

The partial pressure of HFPO decreased with time according to first-order kinetics (Eq. (3)) in each experimental run (Fig. 2). Fig. 3 plots the k_1 values obtained from the data in Fig. 2 against the nominal molar concentrations of NaOH and H_2SO_4 . The k_1 values increased with increasing concentration of NaOH but were almost independent of the concentration of H_2SO_4 in the concentration range examined. Fig. 3 thus suggests that Eq. (4) applies to the hydrolysis of HFPO at NaOH concentrations of 0–50 mM.

$$k_{\text{hyd}} = k_{\text{water}} + k_b [\text{OH}^-] \quad (4)$$

2.2. Evaluation of hydrolysis rate constants of HFPO by fitting to the time series of HFPO partial pressures observed under different reaction conditions

Under the experimental conditions examined, the decrease of gaseous HFPO was apparently limited by mass transfer between the gas and liquid phases (Fig. 1). Using a two-film model to describe the mass transfer process [14] together with Eq. (4) enabled me to simulate the time series of gaseous HFPO as follows:

$$dP_t/dt = -a_1 k_m (K_H P_t - C_D) \quad (5)$$

$$dC_D/dt = a_2 k_m (K_H P_t - C_D) - (k_{\text{water}} + k_b [\text{OH}^-]) C_D \quad (6)$$

where k_m , in $\text{dm}^3 \text{ s}^{-1}$, is the volumetric mass transfer coefficient; K_H , in M Pa^{-1} , is the Henry's law constant of HFPO; and C_D , in M, is the bulk concentration of HFPO in the test solutions. Here the first-order rate constant for the pH-independent hydrolysis of HFPO, k_{water} , is represented in s^{-1} ; the bimolecular rate constant for the hydroxide-catalyzed hydrolysis, k_b , is represented in $\text{M}^{-1} \text{ s}^{-1}$. The constants a_1 and a_2 are defined as follows:

$$a_1 = RT_a / (10^{-3} V_G), \quad (7)$$

$$a_2 = 1/V_L, \quad (8)$$

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