

## 2.016 Rate Constants and C-C Bond Scission Ratios for Hydrolysis or Clay-catalyzed Degradation of 2,2,3-Trifluoro-3-(trifluoromethyl)oxirane (a Fluorinated Epoxide).

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Abstract:

2,2,3-Trifluoro-3-(trifluoromethyl)oxirane (heptafluoropropene oxide, HFPO) is a versatile precursor of fluorinated chemicals. Much information about industrial use of HFPO has accumulated, but little is known about the fate of HFPO after it is released into the environment.

Rate constants for hydrolysis of HFPO were determined at 279–307 K. A reactor with a closed circulation system was used to measure the decrease of HFPO partial pressure while an HFPO-air mixture flowed over a stirred test solution under various experimental conditions. The rate of hydrolysis increased as the  $\text{OH}^-$  concentration increased in an aqueous NaOH solution but was almost independent of the  $\text{H}_2\text{SO}_4$  concentration in aqueous  $\text{H}_2\text{SO}_4$  solutions. Much C–C bond scissioning produced carbon monoxide and trifluoroacetate in aqueous NaOH, but similar scissioning did not in water or aqueous  $\text{H}_2\text{SO}_4$ . The first-order rate constant for the pH-independent hydrolysis ( $k_{\text{water}}$  in  $\text{s}^{-1}$ ) was estimated by simultaneously fitting equations based on a two-film model to the time series of HFPO partial pressures under different experimental conditions. The product of  $k_{\text{water}}$  and the Henry's law constant,  $K_{\text{H}}$  ( $\text{M Pa}^{-1}$ ), 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 suggests that, in the absence of other atmospheric sinks, hydrolysis of HFPO should occur not in clouds but in the ocean (lifetime, some hundreds of years).

Furthermore, clay-catalyzed degradation of HFPO was examined at 283–313 K using the same reactor. The degradation produced carbon monoxide. The degradation rate in dry air was about a tenth times that reported for clay-catalyzed degradation of methyl chloroform under the corresponding experimental condition. The rate decreased with increasing relative humidity; however, the decrease in clay-catalytic activity was not so substantial as that for methyl chloroform.