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Evaluation of the alkaline hydrolysis of HCFC-22 ($CHClF_2$) in a closed-circulation reactor

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ABSTRACT

We evaluated the kinetics of alkaline hydrolysis of HCFC-22 ($CHClF_2$) in hot water, which is a potential method for destruction of this hydrochlorofluorocarbon. Specifically, a $CHClF_2$–air mixture was exposed to different concentrations of aqueous NaOH solution in a closed-circulation reactor, typically at 353 K, and the time course of the gaseous $CHClF_2$ partial pressure was monitored. The decrease in the partial pressure of gaseous $CHClF_2$ exhibited first-order kinetics (rate constant k_1). The main reaction products were F^-, Cl^-, and $HCOO^-$; a minor product was $(COO^-)_2$. The k_1 values obtained when the aqueous NaOH was stirred at high speeds indicated that the rate constant for aqueous reaction of $CHClF_2$ with OH^- (k_{OH^-}) was greater than 0.26 $M^{-1}\,s^{-1}$ at 353 K. The k_1 values increased with increasing OH^- concentration in the range from 0 to 3.5×10^{-2} M; however, at OH^- concentrations greater than 3.5×10^{-2} M, the k_1 value decreased. According to these results, combined with the large, substantiated value of k_{OH^-}, it is expected that alkaline hydrolysis of $CHClF_2$ in aqueous NaOH solution at concentrations of some 10^{-2} M at 353 K would proceed within several minutes if the gas-to-water mass transfer of $CHClF_2$ proceeds efficiently.

1. Introduction

Chlorodifluoromethane (HCFC-22, $CHClF_2$) has been used mainly as a refrigerant in several different applications, as a blend component in foam blowing, and as a chemical feedstock for manufacturing synthetic polymers [1]; however, its emission into the atmosphere is scheduled to be phased out by 2020 in developed countries and by 2030 in developing countries under the Montreal Protocol and its subsequent amendments to protect the stratospheric ozone layer from depletion. Accordingly, discarded equipment containing $CHClF_2$ is collected, and $CHClF_2$ is extracted and destroyed at approved facilities for the destruction of ozone-depleting substances (ODSs).

Base-catalyzed hydrolysis (including alkaline hydrolysis) of $CHClF_2$ is known to proceed with ease, and, to our knowledge, the rate constant for alkaline hydrolysis of $CHClF_2$ in water (i.e., the rate constant for aqueous reaction of $CHClF_2$ with OH^-, k_{OH^-}) has been experimentally determined in four works: k_{OH^-} at 273 K and 293 K [2]; k_{OH^-} at 298 K [3]; k_{OH^-} in temperature range of 298–353 K [4]; k_{OH^-} in temperature range of 313–353 K [5]. The values at ambient temperature of k_{OH^-} reported in these works agreed with one another, but the values at 353 K differed by a factor of 10 as follows [4–6]. McLinden [6] referred to the reported data [4] and represented the temperature dependence of k_{OH^-} (T) in $M^{-1}\,s^{-1}$ by Eq. (1):

$$k_{OH^-}(T) = 1.87 \times 10^8 \exp\left(-\frac{7692}{T}\right) \quad (1)$$

where T (K) is temperature. According to Eq. (1), k_{OH^-} value is calculated to be 6.4×10^{-2} $M^{-1}\,s^{-1}$ at 353 K. On the other hand, one of us reported a k_{OH^-} value of 0.64 $M^{-1}\,s^{-1}$ at 353 K [5]; this value is an order of magnitude greater than the value represented by Eq. (1) and suggests that, in 0.1 M aqueous NaOH solution at 353 K, aqueous-phase $CHClF_2$ can be effectively destroyed in less than 1 min. Alkaline hydrolysis in hot water could thus be a potential method for destroying $CHClF_2$; this method features high energy efficiency and does not require such bulky equipment as the currently approved facilities for the destruction of ODSs. In practice, however, the solubility of $CHClF_2$ in water is so low that most of the $CHClF_2$ is partitioned into the gas phase, thereby resulting in the apparent destruction rates of $CHClF_2$ being substantially lower than those previously mentioned.

In this work, a closed-circulation reactor was used to evaluate the alkaline hydrolysis of $CHClF_2$ in water at 353 K; specifically, we

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determined k_{OH^-} and the dependence of the reaction rate on the OH^- concentration. Our results substantiate the large value of k_{OH^-} previously reported by one of us [5]. Furthermore, the alkaline hydrolysis rate of $CHClF_2$ in aqueous NaOH solution at 353 K was observed to be proportional to the OH^- concentration at OH^- concentrations up to some 10^{-2} M.

2. Results and discussion

2.1. Decrease of gas-phase $CHClF_2$ through alkaline hydrolysis in the closed-circulation reactor

A closed-circulation reactor (Fig. 1) was used to evaluate the alkaline hydrolysis of $CHClF_2$ in water at 353 K. We plotted the

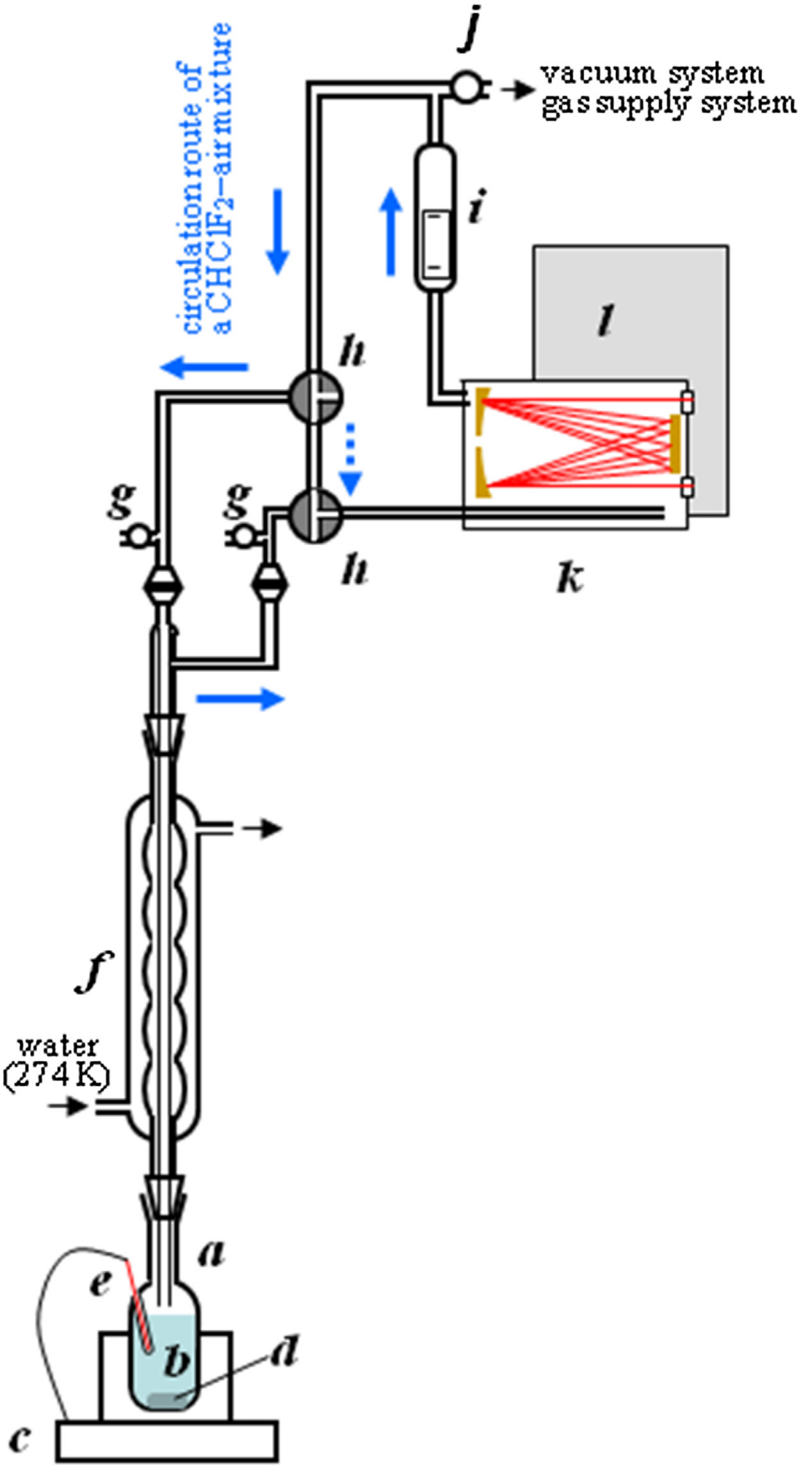

Fig. 1. Schematic of the closed-circulation reactor used in the hydrolysis experiments: *a*, cylindrical liquid cell; *b*, aqueous NaOH solution or deionized water; *c*, aluminum-block tube adapter on a magnetic stirrer with a heater; *d*, stirring bar; *e*, Pt resistance thermometer to provide temperature feedback for controlling the power of the heater of *c*; *f*, Allihn condenser; *g*, vacuum valve for exchanging gas over the solution cell; *h*, valves for changing the circulation route; *i*, magnetically driven glass pump; *j*, vacuum valve to vacuum system or gas supply system; *k*, White-type multireflection cell with a 3 m optical path length; *l*, FTIR spectrometer.