

Deuterium-exchange reaction in a $\text{CF}_3\text{CHBrCl}-\text{D}_2\text{O}$ two-liquid phase system

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Abstract

An alkali-catalyzed hydrogen isotope exchange reaction was studied in a $\text{CF}_3\text{CHBrCl}-\text{D}_2\text{O}$ two liquid phase system. The exchange rate was comparable to that in the $\text{CHCl}_3-\text{D}_2\text{O}$ system previously recognized as the system having the highest exchange rate under alkaline conditions. It was confirmed that CF_3CHBrCl was resistant to decomposition caused by alkali. These properties indicate that CF_3CHBrCl could be a candidate for a working material in laser hydrogen-isotope separation processes.

Introduction

Halogenated methanes and ethanes, especially those containing fluorine, have been considered from their photochemical properties to be promising candidates for working material in the laser isotope separation processes for hydrogen. The T- or D-form compound is selectively decomposed by infrared multiphoton dissociation, and is separated from the H-form compound in the separation process operated in the gas phase [1]. Several materials have been investigated in relation to photochemical properties: for example, CHCl_3 [2], CH_2F_2 [1], CHF_3 [3, 4] and CF_3CHCl_2 [1, 5]. On surveying the working material, the photochemical properties are of great importance. In addition, the isotope exchange ability is also a key factor to be taken into account for the overall process because the deuterium and tritium to be separated are usually in the form of water molecules and these hydrogen isotopes should be transferred into the working material by the exchange process prior to the photochemical separation process. Of course, the rate of isotope exchange of the working material must be high and stability in alkaline solutions is required in the course of the exchange process where basic catalysts are generally employed. Judging from these criteria, out of the photochemically promising materials mentioned above, CHF_3 has a drawback because of its sluggish reaction rate [6]. Although the exchange rate is high with CHCl_3 [7], which is relatively stable in alkaline solutions [8], it is said that CHCl_3 is still decomposed with a significant consumption of hydroxide ion in long-term operations [9]. On the other hand, it is reported that haloethanes with perfluoromethyl groups have relatively high isotope exchange rates [10] and slow decomposition rates [11].

CF_3CDBrCl undergoes selective multiphoton dissociation by CO_2 laser irradiation [12] and the exchange rate is higher than for CF_3CHCl_2 [10]. Therefore, this substance may be a candidate for a working material in laser hydrogen-isotope separation processes. The present study deals with the kinetics of the base-catalyzed hydrogen-isotope exchange in the two-liquid phase system composed of CF_3CHBrCl and D_2O , emphasizing the effect of mass transfer through the interface of the two phases on the exchange rate. The stability of CF_3CHBrCl in alkaline solutions is also investigated. These results are compared to those of the $\text{CHCl}_3\text{-D}_2\text{O}$ system studied in our previous work [9].

Experimental

CF_3CHBrCl (called halothane, hereafter), of 99.9% purity came from Daikin Industry Co., and D_2O , of 99.8% purity, from the CEA Atomic Energy Agency, France. Alkaline solutions were prepared with D_2O and reagent grade sodium hydroxide, which was rinsed with D_2O before dissolution. Halothane and deuterated alkaline aqueous solution, in equal volumes (0.1 dm^3), were introduced into a Pyrex cell of 85 mm inner diameter, and the gas phase over the resulting two-liquid phase system was substituted with nitrogen gas. The halothane phase and the water phase were agitated with two stirrers rotating in opposite directions to each other to ensure uniform solute concentration in the respective phases, and the agitation was performed so that the interface was not disturbed. Experiments were conducted in a water bath thermostatically controlled at 26°C . More details of experiments are described in ref. 9.

The progress of deuterium exchange in the halothane phase was followed by sampling halothane at intervals and analysis using the infrared absorption bands at 1134 cm^{-1} for CF_3CHBrCl and 912 cm^{-1} for the deuterated form. The absorption at 1134 cm^{-1} corresponds to the CH bending vibration [13]. These absorption bands were well separated from each other and from other absorption bands, as shown in Fig. 1.

The ionic species in the water phase were analyzed after some of the exchange runs, in order to evaluate the decomposition of halothane. That is, the concentration of hydroxide ion was determined by titration with hydrochloric acid solution. The concentrations of fluoride and bromide ions were measured with ion electrodes in solutions neutralized with nitric acid. Potentiometric titration of bromide ion was also carried out using a silver ion electrode and silver nitrate solution as the titrant. The results of the bromide concentration from both the methods agreed well. The titration determined not only the concentration of bromide ion but also that of the chloride ion which could not be analyzed by a chloride ion electrode because the electrode was affected by the presence of bromide ion. Products in the halothane phase were also analyzed using a gas chromatograph-mass spectrometer.

(1H, tt, $J = 51.4$ and 5.4 Hz), 6.59 (1H, s), 7.49 (1H, br s); ^{19}F NMR (CDCl_3) $\delta -29.3$ (2F, m), -48.9 (2F, m), -56.9 (2F, dm, $J = 51.4$ Hz).

Reaction of 1b with 5 equimolar amounts of 2-mercaptoethanol

To a stirred solution of 2-mercaptoethanol (25 mmol) and KOH (6 mmol) in 20 ml of ethanol–water (1:3) was gradually added **1b** (5 mmol) at room temperature. After refluxing for 36 h, the reaction mixture was acidified with dilute hydrochloric acid and was extracted with diethyl ether (3×50 ml). The combined organic layers were dried, filtered, and concentrated *in vacuo* to leave a residual oil, whose ^{19}F NMR spectrum showed only one singlet peak due to the trifluoromethyl group. This residue was heated under reflux for 20 h in methanol containing a catalytic amount of sulfuric acid. After the usual work-up, column chromatography of the crude product on silica gel with benzene gave methyl 4,4,4-trifluoro-3,3-bis(2-hydroxyethylthio)butanoate (**7b** methyl ester) in 50% yield as a colorless oil: IR (film) 1740 ($\text{C}=\text{O}$) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.91 (2H, s), 2.99 (4H, t, $J = 6.3$ Hz), 3.67 (3H, s), 3.73 (4H, dt, $J = 5.4$ and 6.3 Hz), 3.90 (2H, t, $J = 5.4$ Hz); ^{19}F NMR (CDCl_3) δ 8.7 (3F, s); MS (m/z) 308 (M^+), 157 (100%).

Reaction of 1a–c with 1.2 equimolar amounts of 2-mercaptoethanol

A mixture of **1** (5 mmol), 2-mercaptoethanol (6 mmol), KOH (6 mmol) and 20 ml of ethanol–water (1:3) was stirred at room temperature for 0.2 h (**1a**), 1 h (**1b**) or 4 h (**1c**). After being acidified, the mixture was extracted with diethyl ether (3×50 ml). The ethereal extracts were dried over anhydrous sodium sulfate, filtered and concentrated under vacuum. Chromatography of the residue on silica gel with chloroform or benzene–chloroform furnished the corresponding 1:1 adduct **6a**, **6b** or **6c** in 85%, 92% or 96% yield, respectively, as an isomeric mixture, in which the ratio of the *Z*- to *E*-isomers was 94:6 for **6a**, 93:7 for **6b** and 92:8 for **6c**. The *Z*-isomers of **6a–c** could be separated by silica-gel column chromatography using benzene–chloroform as eluent.

4,4-Difluoro-3-(2-hydroxyethylthio)-2-butenic acid (6a)

Z-isomer: m.p. 120 to 121 °C; IR (KBr) 1690 ($\text{C}=\text{O}$), 1600 ($\text{C}=\text{C}$) cm^{-1} ; ^1H NMR (300 MHz, CD_3COCD_3) δ 3.13 (2H, t, $J = 6.3$ Hz), 3.75 (2H, t, $J = 6.3$ Hz), 6.30 (1H, t, $J = 1.4$ Hz), 6.67 (1H, t, $J = 54.4$ Hz), 7.20 (2H, br s); ^{19}F NMR (CD_3COCD_3) $\delta -35.7$ (2F, dd, $J = 54.4$ and 1.4 Hz); MS (m/z) no parent to 198, 180 ($\text{M}^+ - \text{H}_2\text{O}$, 35%), 137 (100%).

E-isomer: ^1H NMR (300 MHz, CD_3COCD_3) δ 3.05 (2H, t, $J = 6.3$ Hz), 3.82 (2H, t, $J = 6.3$ Hz), 5.93 (1H, s), 7.20 (2H, br, s), 7.54 (1H, t, $J = 54.1$ Hz); ^{19}F NMR (CD_3COCD_3) $\delta -38.3$ (2F, d, $J = 54.1$ Hz).

4,4,4-Trifluoro-3-(2-hydroxyethylthio)-2-butenic acid (6b)

Z-isomer: m.p. 65 to 66 °C; IR (KBr) 1685 ($\text{C}=\text{O}$), 1595 ($\text{C}=\text{C}$) cm^{-1} ; ^1H NMR (60 MHz, CDCl_3 – CD_3COCD_3) δ 3.11 (2H, t, $J = 6.0$ Hz), 3.82 (2H,

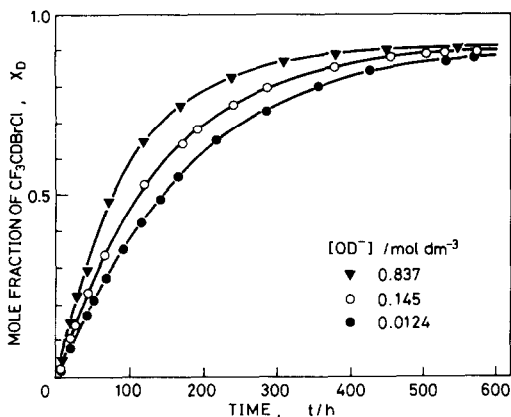
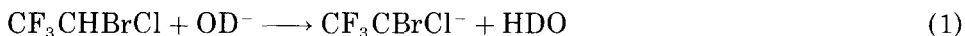


Fig. 2. Time variation of the deuterium fraction of CF_3CHBrCl under given alkaline concentrations.

run, and was close to the theoretical value (0.92) for reaction (3) under the present experimental conditions. The durability to decomposition is attributed to the greater stability of perfluoromethyl groups in basic media over other halogen-containing methyl groups [15].

Although the decomposition of halothane was minor in this system, analyses were conducted for the halothane and the water phases after the exchange run to inspect the reaction products. A very small peak other than halothane was observed in the gas chromatogram for the halothane phase sample; from the mass spectroscopy this was determined to be $\text{CF}_2=\text{CBrCl}$, produced by the dehydrofluorination of halothane. In the water phase, an appreciable amount of fluoride ion with only traces of bromide and chloride ions was detected (Table 1). According to Hine and co-workers [11], dehydrofluorination proceeds through two steps:



Thus, the predominant reaction consuming the alkaline catalyst is the dehydrofluorination, but the rate is very slow compared to the isotope exchange rate.

Hine *et al.* [7] reported that the isotope exchange rate between CDCl_3 and H_2O was controlled by the exchange reaction under homogeneously mixing conditions. On the other hand, Maienschein and Barry pointed out that mass transfer could be rate controlling in the CDCl_3 - D_2O two-phase system when the alkaline concentration was high and/or solution agitation was insufficient [14]. Quantitative analysis has been conducted by Iwasaki *et al.* [9] for the CHCl_3 - D_2O system. They obtained rate constants for the exchange reaction and the mass-transfer steps. The

TABLE 1

Concentrations of ions in the water phase after the exchange experiment (in mol dm⁻³)

[OH ⁻]		[F ⁻]	[Br ⁻]	[Cl ⁻]
initial	consumption			
0.114 ^a	0.026	0.0042	0.00052	0.00055
0.455 ^b	0.038	0.012	0.00040	0.00049
1.00 ^b	0.030	0.0083	0.00086	0.0011

^aMild stirring for 620 h at 26 °C, preventing mixing of the halothane and water phases (see Experimental section).

^bHomogeneous mixing for 24 h at room temperature using halothane and water of equal volumes (10 cm³).

initial reaction rate for the hydrogen isotope exchange is described as follows [9]:

$$1/r = b/(k_{tr}Sa_0) + b/(k_{ex}a_0V[\text{OD}^-]) \quad (5)$$

where r is the initial reaction rate, $(dX_D/dt)_{t=0}$; a_0 is the halothane concentration in the water phase; V is the volume of the water phase; b is the number of moles of halothane in the halothane phase; S is the interfacial area of the two phases; and k_{tr} and k_{ex} are the rate constants of the mass transfer through the interface and of the isotope exchange reaction, respectively.

Figure 3 illustrates the initial hydrogen-isotope exchange rate as a function of OD⁻ concentration. Equation (5) describes the experiments well if the alkaline concentration is not high. Although the parameters in

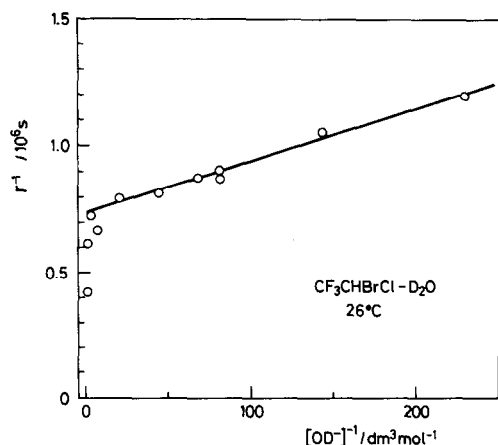


Fig. 3. Reciprocal plots of the initial exchange rate as a function of the alkali concentration.

eqn. (5) are mostly given by the experimental conditions, the solubility of halothane in water must be determined as a function of the alkaline concentration. A published result ($1.8 \times 10^{-2} \text{ mol dm}^{-3}$) is available in ref. 16, but the experimental conditions are unclear. The solubility was measured with solutions of various alkaline concentrations according to the gas chromatographic method described by Yokoyama *et al.* [17]. The results are shown in Fig. 4. The solubility in pure water was $(2.09 \pm 0.09) \times 10^{-2} \text{ mol dm}^{-3}$ at 26°C , and the alkaline concentration dependence satisfied Setschenow's relation [18] with a salting coefficient of 0.345.

Using these results, the rate constants of the mass-transfer and the exchange reaction were evaluated (Table 2) with the alkaline concentration range lower than 0.1 mol dm^{-3} , where the linear relationship $1/r$ vs. $1/[\text{OD}^-]$ holds. The rate constants were found to be close to those in the $\text{CHCl}_3\text{-D}_2\text{O}$ system. The first term of the right-hand side in eqn. (5) is related to the mass transfer and is independent of the concentration of hydroxide ion. On the other hand, the second term corresponds inversely with the exchange reaction rate, and increases with the concentration. The exchange reaction rate and the mass-transfer rate are equal to each other at the hydroxide ion concentration of $2.7 \times 10^{-3} \text{ mol dm}^{-3}$. That is, the overall isotope exchange rate is controlled by the exchange reaction step in the hydroxide ion concentration range lower than $2.7 \times 10^{-3} \text{ mol dm}^{-3}$, while the mass-transfer step through the interface becomes rate controlling when the alkaline concentration increases.

The exchange rate in the $\text{CF}_3\text{CHBrCl-D}_2\text{O}$ system is about one-half that in the $\text{CHCl}_3\text{-D}_2\text{O}$ system, whereas the rate constants in the two systems are about the same. The low exchange rate is mainly attributed to the low solubility of halothane in water compared to chloroform, because the rate increases with the solubility. However, this drawback of the halothane system is overcome by its durability to bases, since chloroform is decomposed in alkaline solution more easily than halothane, resulting

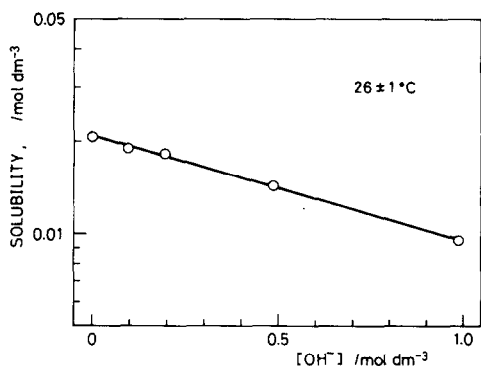


Fig. 4. Solubility of CF_3CHBrCl in alkaline solutions at 26°C .

TABLE 2

Rate constants in the hydrogen-isotope exchange reaction at 26 °C

	CF ₃ CHBrCl-D ₂ O	CHCl ₃ -D ₂ O ^a
k_{ex} (dm ³ mol ⁻¹ s ⁻¹)	0.223 ± 0.004	0.231 ± 0.013
$k_{\text{tr}} \times 10^5$ (m s ⁻¹)	1.08 ± 0.01	1.07 ± 0.03
a_0 (mol dm ⁻³)	0.0209	0.059

^aRef 9.

in the consumption of hydroxide ion, and then a decrease in the exchange rate during operation if the alkaline concentration is in the range where the rate is controlled by the exchange reaction. As a consequence, the halothane system could be a promising candidate for a working material in laser hydrogen-isotope separation processes.

Conclusions

The hydrogen-isotope exchange in a CF₃CHBrCl-D₂O system was studied in the two-liquid phase system in order to survey the possibility of the application of this system to laser hydrogen-isotope separation processes. The exchange rate was controlled by the exchange reaction step at low alkaline concentrations, but the interfacial mass-transfer step became rate controlling when the concentration of hydroxide ion increased. The initial exchange rate was about one-half of that in the CHCl₃-D₂O system, mainly due to the low solubility of halothane in water. On the other hand, halothane was resistant to basic catalysts compared to chloroform. Therefore, halothane would be appropriate from the viewpoint of isotope exchange as a working material for utilization in laser hydrogen-isotope separation processes.

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