

Preparation and physicochemical properties of *F-tert*-butyl alkyl ethers

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Abstract

As a part of studies on the development of CFCs alternatives, *F-tert*-butyl alkyl ethers [(CF₃)₃COME and (CF₃)₃COEt] were prepared and their basic physicochemical properties were determined. They were prepared by alkylation of isolated (CF₃)₃CONa with dialkyl sulfates [(RO)₂SO₂; R = CH₃, C₂H₅] with good yields. It was found that the yields were affected by the kind of polyglymes used as a solvent. Tetraglyme was a much better solvent than diglyme for dissolving (CF₃)₃CONa, this fact being ascribed to the number of intramolecular oxygen atoms in polyglymes for coordination to Na⁺. A correlation between the structure of the *F-tert*-butyl group of the ether, C₄F₉OR, and some physical properties was observed, in which an ether having an *F-tert*-butyl group has a lower boiling point and gaseous thermal conductivity compared with that having an *F-n*-butyl group. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

It is common knowledge that the depletion of the stratospheric ozone layer by CFCs, HCFCs and halons etc. has become a serious global environmental problem [1]. As a counter measure against this problem, we have been engaged in the development of hydrofluoroethers (HFEs) as alternatives to CFCs as refrigerants, blowing agents, solvents and so on [2–8]. Especially in the case of alternatives for blowing agents, the property of low thermal conductivity in the gaseous state is important, since energy efficiency depends directly on the thermal insulation of foams. We recently reported that the gaseous thermal conductivity of HFEs was lower than that of other promising alternatives such as HFC-245fa (CF₃CH₂CHF₂) and cyclopentane. Particularly, *F-tert*-butyl alkyl ethers such as (CF₃)₃COME (**1**) and (CF₃)₃COEt (**2**) showed the lowest gaseous thermal conductivity of the HFEs [6,8].

Here we describe the efficient synthesis and determination of the physicochemical properties of **1** and **2**. Compound **1**

was previously prepared by reaction of (CF₃)₃COHgCl with MeI (Yield = 73%) [9].

2. Results and discussion

2.1. Preparation of *F-tert*-butyl methyl ether (**1**) and *F-tert*-butyl ethyl ether (**2**)

Two methods were used for the preparation of **1** and **2**. The first method involves the reaction of in situ generated potassium *F-tert*-butoxide [(CF₃)₃COK] (**3**) with diethyl sulfate in ethanol. The second method involves the reaction of isolated sodium *F-tert*-butoxide [(CF₃)₃CONa] (**4**) with dialkyl sulfate [(RO)₂SO₂; R = Me, Et] in polyglyme. These results are summarized in Table 1. In the first method where *F-tert*-butyl alcohol (**5**) was used as a reactant, we tried to alkylate **3**, which is formed in situ by treating **5** with KOH in an aprotic solvent such as diglyme, with dialkyl sulfate. However, this attempt was unsuccessful, as KOH was sparingly soluble in diglyme. In order to make a solution of KOH, ethanol was used as a solvent for the preparation of **2**, because diethyl sulfate, which is used as an alkylating agent, is an ester of sulfuric acid and ethanol (Eq. (1)). However,

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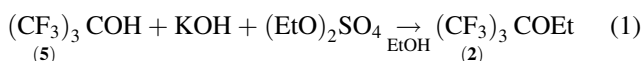
Table 1
Result of the reactions

Run #	Reaction	Solvent	Yield of (CF ₃) ₃ COR %		
			¹⁹ F-NMR GC ^a isolated		
1	(CF ₃) ₃ COH + KOH + (EtO) ₂ SO ₄	EtOH	10		
2	(CF ₃) ₃ CONa + (EtO) ₂ SO ₄	Diglyme	97.5 ^b	99.9	60
3	(CF ₃) ₃ CONNa + (EtO) ₂ SO ₄	Tetraglyme	100	99.9	93
4	(CF ₃) ₃ CONa + (MeO) ₂ SO ₄	Tetraglyme	100	99.9	93

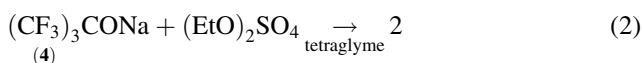
^a Percent area on gas chromatogram after washing with aqueous NaOH.

^b The rest was (CF₃)₃COH.

even under such modified reaction conditions, the yield of **2** was very low (yield = 10%) according to the analysis by ¹⁹F-NMR.



In the second method where an isolated **4** was used as a reactant, polyglyme was used as a solvent. Previously, alkali metal *F-tert*-butoxides were prepared by reaction of **5** with appropriate metals or metal hydrides in anhydrous ether [10–12]. In this study, **4** was prepared by a simpler method, consisting of treatment of **5** with aqueous NaOH, followed by evaporation to dryness. The reaction temperature was kept at 0°C by cooling in order to minimize the possible formation of highly toxic perfluoroisobutene (PFIB). Compound **4** dissolved well in polyglyme, and the reaction with diethyl sulfate proceeded smoothly in this type of solvent. However, when diglyme was used in this reaction, complete separation of the product from the solvent was difficult. The presence of a significant portion of diglyme in the distillate collected by flash distillation caused its emulsification upon washing with aqueous NaOH. When tetraglyme was used instead of diglyme, highly pure product **2** could be collected in a quantitative yield after flash distillation followed by washing with aqueous NaOH (Eq. (2)).



2.2. Solubility of (CF₃)₃CONa (**4**) in polyglyme

It was found that there were remarkable differences in the solubility of **4** depending on the kind of polyglyme used. At ambient temperature (25°C), the solubility of **4** increased with an increase in the chain length of the polyglyme. At 75°C (reaction temperature), triglyme and tetraglyme made **4** extremely soluble, as compared with diglyme (Table 2). The reason for the increased solubility of polyglymes having more than three oxygen atoms for **4** is ascribed to the increased coordination of the oxygen of solvent molecules with Na⁺. Thus, tetraglyme is a preferred solvent to diglyme due to the higher solubility of **4** as well as easier separation of the product.

Table 2
Solubility of (CF₃)₃CONa in polyglyme

Solvent	B.p. (°C)	Solubility (g/100 g) ^a	
		25°C	75°C
Diglyme	162	2	12
Triglyme	216	27	82
Tetraglyme	275	55	83

^a(CF₃)₃CONa(g)/polyglyme (100 g).

2.3. Basic physicochemical properties of *F-tert*-butyl methylether **1** and **2**

The basic physicochemical properties of **1** and **2** were found to be similar to those of isomeric *n*-C₄F₉OR (R = Me, and Et, respectively), except for boiling point and gaseous thermal conductivity, which were important properties for blowing agents (Table 3). Generally, gaseous thermal conductivity is related to molecular weight [8,13–20]. Therefore the lowering of the gaseous thermal conductivity of **1** and **2** as compared with that of corresponding *n*-C₄F₉OR is ascribed to the difference in the structure of the *F*-butyl group. It is considered that lowering of both boiling point and gaseous thermal conductivity by introducing the *F-tert*-butyl group in place of the *F-n*-butyl group in the C₄F₉OR structure, is advantageous for use as a blowing agent.

3. Experimental details

All reactions were performed in glass reactors. ¹H-, ¹³C- and ¹⁹F-NMR spectra (chemical shifts in ppm from internal reference, TMS, CDCl₃ and CFC-11) were recorded on a JEOL LAMBDA (300 MHz) spectrometer with CFH probe.

3.1. Preparation of **1** using isolated **4**

Dimethyl sulfate (0.2 mol) was added dropwise to a stirred solution of **4** (0.1 mol) dissolved in tetraglyme (500 ml) over a 90 min period at 70°C in a 1500 ml glass reactor fitted with a reflux condenser. After the addition of dimethyl sulfate, the reaction mixture was heated to 90°C for 60 min. The product was then collected by flash

Table 3
Physicochemical properties

Sample	B.p. K	Gaseous thermal conductivity ^a (mW/m K)	Viscosity (mPa s)	Specific volume (Kg/m ³)	Surface tension (mN/m)	Specific heat (kJ/kg K)	Heat of vaporization (kJ/kg @ b.p.)	SP value (MPa ^{1/2})
(CF ₃) ₃ COMe	326.79	13.75	0.932	1558.5	13.92	1.156	121.1	13.5
(CF ₃) ₃ COEt	340.27	13.65 ^b	0.747	1450.2	13.78	1.191	119.2	13.0
(CF ₃) ₃ COMe	333.20 ^c	14.69	0.648 ^c	1502.6 ^c	13.59 ^c	1.178 ^c	123.6 ^c	13.4
n-C ₄ F ₉ OEt	350.04 ^c	–	0.643 ^c	1416.8 ^c	13.60 ^c	1.213 ^c	123.4 ^c	13.1

^aMeasured at 70°C.

^bMeasured at 0.09 MPa (others at normal pressure).

^cFrom [4,5].

distillation at room temperature to 70°C under reduced pressure. After successive washing with 10% aqueous NaOH and deionized water, pure **1** (23.3 g) was obtained as a transparent organic liquid with a yield of 93% (isolated yield). The spectral data for **1** are as follows. ¹H-NMR: δ = 3.83 ppm (s, 3H, CH₃), ¹⁹F-NMR: 70.90 ppm (bs, 9F, CF₃), ¹³C-NMR ¹³C- $\{^1\text{H}\}$ - $\{^{19}\text{F}\}$: 56.92 ppm (CH₃), 80.58 ppm (*tert*-C), 121.09 ppm (CF₃). MS (EI): *m/z* = 250 M⁺ (0.77), 231 [M-F]⁺ (9.2), 219 (CF₃)₃C⁺ (0.85), 181 (CF₃)₂(CH₃O)C⁺ (base peak), 69 (CF₃⁺) (91), 15 CH₃⁺ (33).

3.2. Preparation of **2** using isolated **4**

The reaction and purification procedures were the same as those described for the preparation of **1** except that diethyl sulfate was used instead of dimethyl sulfate as the alkylating agent. The yield of **2** was 60% when diglyme was used as solvent and 93% when tetraglyme was used as solvent. The spectral data for **2** are as follows. ¹H-NMR: δ = 4.07 ppm (q, 2H, CH₂, J = 7.0 Hz), 1.32 ppm (t, 3H, CH₃, J = 7.0 Hz). ¹⁹F-NMR: 71.13 ppm (bs, 9F, CF₃). ¹³C-NMR: ¹³C- $\{^1\text{H}\}$ - $\{^{19}\text{F}\}$: 15.27 ppm (CH₃), 65.95 ppm (CH₂), 80.21 ppm (*tert*-C), 120.73 ppm (CF₃). MS (EI): *m/z* = 264 M⁺ (0.56), 219 (CF₃)₃C⁺ (0.05), 195 (CF₃)₂(CH₃CH₂O)C⁺ (14), 69 (CF₃⁺) (16), 29 CH₃CH₂⁺ (base peak), 15 CH₃⁺ (2.2).

3.3. Preparation of **2** using *in situ* generated (CF₃)₃COK (**3**)

A reaction mixture of KOH (22 mmol) and (CF₃)₃COH (**5**) (20 mmol) in ethanol (20 ml) was stirred over a 30 min period at 50°C in a 100 ml round-bottom flask fitted with a reflux condenser. After the dropwise addition of diethyl sulfate (22 mmol), the reaction mixture was gradually heated to 70°C and was kept at this temperature for 3 h. The mixture was cooled to room temperature while stirring. The formation of **2** was analyzed by ¹⁹F-NMR (yield = 10%). No further optimization of the reaction conditions was attempted.

3.4. Preparation of (CF₃)₃CONa (**4**)

An aqueous solution of **5** (1 mol) in water (1 mol) was added dropwise to a stirred aqueous solution (240 g) of NaOH (1 mol) in a 1000 ml round bottom-flask over a 30 min period at 0°C. This mixture was stirred at ambient temperature for 30 min, and then evaporated to dryness under a vacuum, yielding **4** as a white solid (255 g) quantitatively.

3.5. Solubility measurements of **4** in polyglymes

The solubility of **4** in three polyglymes (diglyme, triglyme and tetraglyme) at 25°C and 75°C was measured using an ion chromatograph (Yokogawa PCH-035, SCH-125) and an aqueous solution of nitric acid (6 mM) was used as the carrier liquid. The top clear layer of the saturated liquid of **4** was analyzed by means of ion chromatography. The saturated concentration was determined from the calibration line. The values were verified by an experiment which consisted of leaving the sample standing for one night with the calculated concentration at measuring temperature. The results are summarized in Table 2.

3.6. Measurement of basic physicochemical properties of **1** and **2**

Physicochemical properties, including boiling point, viscosity, specific volume, surface tension, gaseous thermal conductivity, and specific heat, were measured for **1** and **2**. A comparison of the data for physical properties of **1** and **2** with those of *F*-*n*-butyl methyl ether and *F*-*n*-butyl ethyl ether is summarized in Table 3. The procedure for the measurement of each of these physical properties is described below.

3.6.1. Boiling point

The boiling point was measured according to the isoteniscope method [21]. The isoteniscope, made of Pyrex glass, was attached to a pressure-controlled measurement system and placed in a thermostated bath. The sample temperature was regarded as equal to the temperature of the bath

measured with a platinum resistance thermometer with a precision of ± 0.01 K.

3.6.2. Viscosity

Viscosity was measured at 296 K with an Ubbelode-type automatic viscometer. The temperature was maintained constant within 296.00 ± 0.01 K. No kinetic energy correction was necessary. The viscometer was calibrated with a standard liquid of *o*-xylene. The viscosity values of *o*-xylene used were 0.809 mPa s at 293.15 K, 0.708 mPa s at 303.15 K, and 0.625 mPa s at 313.15 K [22]. The flow time of each sample was measured at 296.00 K and converted into dynamic viscosity. The experimental uncertainty was $\pm 4\%$.

3.6.3. Specific volume

Specific volume was measured at 296 K with a Lipkin–Davison type pycnometer made of glass immersed in a water bath. First, the volume of the pycnometer containing about 5 cm^3 was determined with degassed pure water. Next, the sample was charged into the pycnometer and the mass was determined using an AEU-210 Shimadzu electronic balance with a precision of ± 0.1 mg. The pycnometer was immersed in the water bath and the temperature of the thermostated water bath was measured with a mercury thermometer with a precision of ± 0.02 K. The weight of the sample was determined by buoyancy effects. The experimental uncertainty was $\pm 0.01\%$.

3.6.4. Surface tension

Surface tension was measured by means of a Cahn 2000 electrobalance based on the ring method of de Nouy. The force was measured in a Pyrex glass vessel with a jacket for circulating thermostated water at $296 \text{ K} \pm 0.02$ K. The mean circumference (L) of the platinum ring was 5.956 cm. Force was measured with the Cahn 2000 electrobalance with a precision of ± 0.1 mg. Surface tension (T) was calculated by the following equation:

$$T = \frac{mgF}{2000L}$$

where m is maximum mass on a mg basis, g is acceleration due to gravity 979.7 cm/s^2 , and F is a correction factor [23]. The experimental uncertainty was ± 0.1 mN/m.

3.6.5. Gaseous thermal conductivity

The gaseous thermal conductivity of $n\text{-C}_4\text{F}_9\text{OMe}$ was measured by the steady state coaxial cylinder method using a calorimeter (Setaram, C-80D) in the same manner as described in previous reports [6,8], where the data of $(\text{CF}_3)_3\text{COMe}$ and $(\text{CF}_3)_3\text{COEt}$ were reported. After being flushed with sample gas twice, the co-axial cylinder cell, which was heated up to the measuring temperature (70°C), was filled up with a sample gas. After the cell reached thermal equilibrium, constant energy (100 mW) was supplied to the heater for 1 h. The detected heat flux was

converted into thermal conductivity using the following empirical equation.

$$\lambda = \frac{-S + a}{bS + c}$$

where λ is the thermal conductivity (mW/m δ K) and S is the detected heat flux (μV)

In this study, measurements were performed on a relative basis. The equipment constants, a , b , and c , were calibrated against seven reference gases (H_2 , CH_4 , air, N_2 , Ar, CO_2 and CFC-11), whose reference thermal conductivity values were collected from reliable data sources [24–30]. The validity of the calibration curve was examined by HCFC-141b. The gaseous thermal conductivity of HCFC-141b obtained in this study agreed with the result by the transient hot-wire method [31] to within 3%. Judging from this result and the reproducibility of measurement, the uncertainty of thermal conductivity obtained was estimated to be less than 4%.

3.6.6. Specific heat

Specific heat (C_p) was measured at 296.00 K by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC 2 [32]. Three DSC scans of the sample, the blank (empty pan), and the standard (sapphire disc about 40 mg) were measured under the same conditions. Specific heat was calculated from the difference in DSC signals at the final temperature (296 K) under consideration of sample size, standard C_p value, scanning rate (10 K/min), and correction of pan size. The experimental uncertainty was $\pm 2\%$.

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