A novel synthesis of trifluoromethyl fluoroformate from trifluoromethyl hypofluorite and carbon monoxide in the presence of fluorine gas

Libin Du [a], Darryl D. DesMarteau [b,*]

[a] Department of Chemistry, The University of North Carolina, Chapel Hill, NC 27599, USA
[b] Department of Chemistry, Clemson University, Clemson, SC 29634, USA

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ABSTRACT

Trifluoromethyl fluoroformate is prepared through a radical reaction between CF_3OF and CO initiated by elemental fluorine. The reaction could be integrated into a continuous synthesis process. This method represents a convenient synthesis of the title compound under mild condition.

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1. Introduction

The preparation of trifluoromethyl fluoroformate, $CF_3OC(=O)F$ (**1**), was first achieved through a photochemical reaction of CF_3OF and CO initiated by a Hg arc filtered through Pyrex glass and H_2O [1]. A pyrolytic version of the reaction was also mentioned therein, but without any detail. A later patent described the preparation of **1** as the dimer of carbonyl fluoride, COF_2 (**2**), using a variety of catalysts [2]. It was also isolated as a minor product or the rearranged product in a variety of other reactions [3–9]. The efficient preparation of **1** is of considerable interest currently as the key intermediate to a vinyl ether, $CF_3OCF_2OCF=CF_2$, whose copolymers have been used to formulate novel fluoroelastomers with very low glass transition temperatures [10–17]. These properties are essential in certain areas such as aerospace as exemplified by the discovery space shuttle disaster which was caused by failure of elastomer seals at low temperature [17]. The fluoroformate **1** can be easily decomposed by strong nucleophiles such as fluoride ion [18,19], so the vinyl ether, $CF_3OCF_2OCF=CF_2$, could only be prepared through photofluorination of **1** with elemental fluorine followed by addition to $CFCl=CFCl$ and

dehalogenation [20]. However, the current synthetic route to **1** is inefficient and the reaction conditions can easily decompose **1** due to the possible generation of fluoride ions [10,11,14].

Herein, we report an alternative synthetic pathway to prepare **1** through a facile radical reaction between CF_3OF and CO initiated by elemental fluorine. Compared with the previous reported processes [1,2,10–15], this route does not require high temperatures or UV radiation, and can occur spontaneously at or below room temperature. The reaction is rapid and has potential for integration into a continuous process which may be difficult for other previously reported routes.

2. Results and discussion

In the photolysis and pyrolysis of CF_3OF and CO, CF_3OCO radicals formed through combination of a CF_3O radical and CO were proposed in the chain reaction forming **1** [1]. However, the cleavage of O-F bond requires either high temperatures or UV irradiation, and the yields were relatively low with high concentrations of side products such as COF_2 (**2**) [10,11,14]. The formation of CF_3OCO radicals are also expected to compete with the decomposition of CF_3O radical into COF_2 and F atoms which may in part be responsible for the generation of COF_2 as a side product [1]. In order to carry out the reaction under milder conditions such as room temperature, providing an easily generated radical to initiate the fast chain reaction was considered.

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* Corresponding author. Tel.: +1 864 656 1251; fax: +1 864 656 2545.
 E-mail addresses: dlibin@email.unc.edu (L. Du), fluorin@clemson.edu
(D.D. DesMarteau).
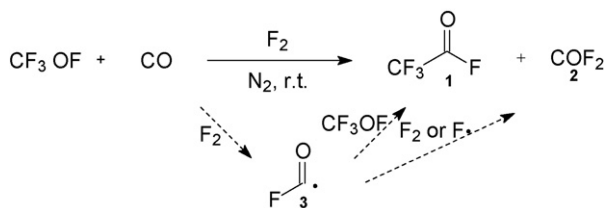
Scheme 1. The radical reaction between CF_3OF and CO initiated by F_2.
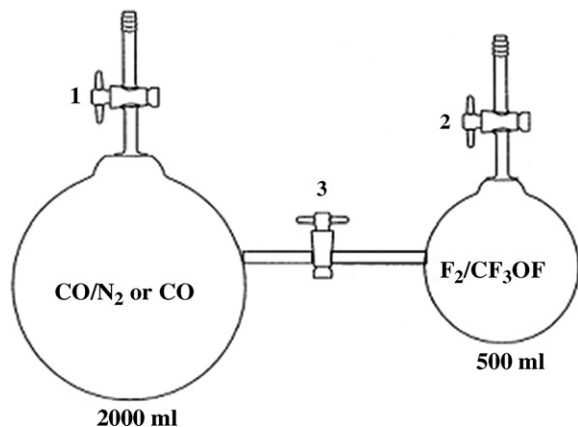
Fig. 1. Static system used in the reaction between CF_3OF and CO initiated by F_2.

Table 2
Reactions of CF_3OF and CO initiated by F_2 with unequal pressures in the flasks

Entry	CF_3OF/F_2 in the small flask		CO in the big flask		$CF_3OC(O)F$[a] (mmol)	Yield[b] (%)	COF_2[a] (mmol)
	mmol	atm	mmol	atm			
1	10/1.5	0.57	78.5	0.96	0.9[c]	9.0	4.3
2	10.2/0.4	0.52	76.9	0.94	0.9[d]	8.8	0.05
3	10.1/0.6	0.52	20.4	0.25	0.4[d]	4.0	0.2

[a] Based on the integration on ^{19}F NMR spectra.
[b] The yields were calculated based on the amount of CF_3OF.
[c] Contaminated with some unknown side products.
[d] Pure.
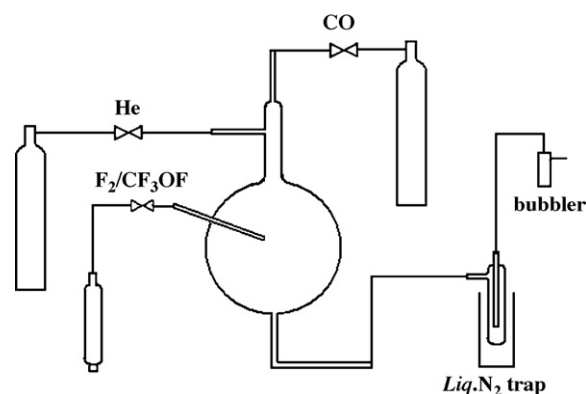
Fig. 2. The 1 L flow system used in the reaction of CF_3OF and CO initiated by F_2.

A fluoroformyl radical, $FC(=O)$ (**3**), generated from the facile reaction of F_2 and CO was reported to be responsible for the efficient preparation of $FC(=O)OO(=O)CF$ through a fast chain reaction at room temperature [21]. We expected that this fluoroformyl radical would also initiate a chain reaction between CF_3OF and CO, under milder conditions (see Scheme 1).

The reaction was first attempted in a closed system (see Fig. 1) with nitrogen gas being used as a diluent in the reaction. Carbon monoxide was added in excess compared to CF_3OF in order to facilitate the desired reaction to form **3** and **1** and minimize the side product **2**. (*Caution*: the reaction between fluorine and carbon monoxide can be explosive, so it must be carried out in a controlled manner!) A relatively high yield of 18% was obtained in a run with a 20/3 ratio of CF_3OF to F_2 (entry 1 in Table 1). The amount of product **1** was approximately equal to the amount of the fluorine feed in entry 1, so it was initially thought that the yield was closely related to the amount of elemental F_2. Increasing the ratio of F_2 to CF_3OF with the intent to improve the yield in the second run, resulted in a violent reaction in which **1** was not even detected as a product (entry 2). On the other hand, the lower ratio of F_2 to CF_3OF in entry 3 generated a negligible amount of COF_2, but gave a much lower yield of **1**.

The abstraction of a CF_3O radical from CF_3OF by **3** appears to be much less energetically favored than its reaction with F atoms or molecular fluorine. A large excess of CO is always needed to trap F atoms before they can combine with **3** to form COF_2 (see Scheme 1). A high ratio of CF_3OF to F_2 increases the probability of **3** reacting with CF_3OF rather than F_2 (Scheme 1). The effect of the amount of N_2 diluent on the reaction was not studied.

In Table 1 the initial pressures in the two flasks were nearly the same and the mixing of the gases on opening the connecting valve was assumed to be slow. In Table 2 runs were conducted without N_2 diluent with a higher pressure in one of the flasks. The assumption was that the gases would mix more rapidly. Contrary to expectations, higher yields of **1** were not observed.

Based on the static reactions in Tables 1 and 2, a flow reaction was carried out in a 1 l glass apparatus shown in Fig. 2. The low conversion (3%, see Section 3) was disappointing but we expect that this reaction could be greatly improved by reactor design and varying reactant concentrations. The experiments described above were run at room temperature without any mechanical mixing. The reaction could easily become explosive as the heat dissipation was inefficient under this condition. However, in a possible industrial setup [18], the reaction could be run in an inert solvent with efficient agitation. The reaction could also be run at lower temperatures which should help to suppress the side reactions such as the one between F_2 and CO to generate COF_2. Both CO and CF_3OF would be in a large excess compared with F_2. In such a system, the COF_2 could be recycled to CF_3OF and un-reacted CF_3OF

Table 1
Reactions of CF_3OF and CO initiated by F_2 with equal pressures in the two flasks

Entry	CF_3OF (mmol)	F_2 (mmol)	CO (mmol)	N_2 (mmol)	$CF_3OC(O)F$[a] (mmol)	Yield[b] (%)	COF_2[a] (mmol)
1	20.1	3.1	40.8	50.9	3.6	18.0	>0.7
2	19.2	11.9	60.5	30.8	–	–	>10.0
3	16.0	1.6	32.4	34.2	0.7	4.2	Trace

[a] Based on the integration on ^{19}F NMR spectra.
[b] The yields were calculated based on the amount of CF_3OF.

would be easily recycled, so the single-cycle yield might not be critical. An optimized system of this type would require considerable engineering. We made no attempt in this study to optimize this process but simply wanted to demonstrate that a flow system with potential for scale-up was viable.

In summary, the preparation of $CF_3OC(=O)F$ has been achieved at room temperature through a radical reaction between CF_3OF and CO initiated by the presence of elemental fluorine. This reaction has potential for scale-up in a continuous flow system.

3. General experimental procedures

3.1. Instruments

^{19}F NMR spectra were recorded on a JOEL FT/NMR at 282.8 MHz. The samples were sealed in a 4-mm glass tube with CCl_4 as solvent and $CFCl_3$ as reference. The 4-mm tube was inserted into a standard 5-mm NMR tube for measurement. The lock D_2O was added to the outer tube. Infrared spectra were recorded on a PerkinElmer spectrum 2000 FTIR. The sample was contained in a 10 cm glass cell fitted with a Kontes glass-Teflon valve and AgCl windows held in place with Halocarbon 1500 wax.

3.2. Apparatus and reagents

The reactions were carried out either in a static (Fig. 1) or a flow systems (Fig. 2). The closed system was comprised of two bulbs sized at 2000 and 500 ml, respectively, connected by a Kontes glass-Teflon valve. The reactor was dried at 100 °C in an oven followed by an overnight evacuation for 10–12 h at 22 °C. The flow reactor was first dried at 100 °C in an oven followed by purging with helium gas for 50 min at 22 °C.

The preparation of CF_3OF was carried out according to the standard literature procedure [22]. Fluorine gas was purchased from Air Products and Chemicals and passed through a NaF scrubber before use. (Caution: fluorine and CF_3OF are extremely reactive and toxic and must be handled with care!) Phosgene, CO and CsF were used as received. Carbonyl fluoride was prepared from phosgene by reaction with NaF in CH_3CN at 40–50 °C.

3.3. Typical procedure

3.3.1. Preparation of $CF_3OC(=O)F$ in the closed system

In a typical reaction, 40.8 mmol CO and 50.9 mmol N_2 were first added to 2 L bulb of the closed system (Fig. 1). A premixed sample of 20.1 mmol CF_3OF and 3.1 mmol F_2 was then added to the smaller 0.5 L bulb. (Caution: the reaction between fluorine and carbon monoxide can be explosive and must be carefully controlled!) The inside pressure of the 2 L bulb was calculated to be 1.14 atm vs. 1.16 atm in the 0.5 L bulb. With the reactor at 22 °C, the valve connecting the two bulbs was opened slowly and the rector was kept at room temperature for 48 h behind a shield. The contents of the reactor bulbs were then collected through traps at −135, −146 and −196 °C. $CF_3OC(=O)F$ (2.1 mmol) was collected in the −135 °C trap. The rest of the chemicals collected in the other two traps were CF_3OF contaminated with $CF_3OC(=O)F$ and COF_2. The latter was then passed through three traps at −130, −145 and −196 °C. A ca. 1.6 mmol of $CF_3OC(=O)F$ contaminated with a little COF_2 was collected in the −130 °C trap. Carbonyl fluoride contaminated with $CF_3OC(=O)F$ (0.7 mmol) was collected in −145 °C trap and 16.1 mmol of CF_3OF contaminated with a small amount of COF_2 was collected in the −196 °C trap. The overall isolated yield of

$CF_3OC(=O)F$ was 18.4%. The characteristic properties and spectral values of $CF_3OC(=O)F$ agreed with the literature [1,8]. ^{19}F NMR (CDCl$_3$): $\delta = -60.5$ ppm (d, 3F, $^3J_{F-F} = 9.9$ Hz, CF$_3$), $\delta = -13.5$ ppm (q, 1F, CF).

3.3.2. Preparation of $CF_3OC(=O)F$ in the flow system

The reaction was carried out in a flow system (Fig. 2). Helium and CO gas cylinders were attached to the system through two calibrated Gilmont gas flow meters. A passivated Monel bomb reactor containing 61 mmol CF_3OF and 10.2 mmol of F_2 was also attached to system through a digital Hastings Fluorine mass flowmeter. The gas outlet was attached to an oil bubbler containing Krytox® fluids through a collection trap maintained at −196 °C. First, the system was purged with helium gas at 54 ml/min for 50 min followed by CO at 20 ml/min for another 30 min. The bomb reactor containing the mixture of CF_3OF and F_2 was then slightly opened and the flow rate was adjusted to 15 ml/min initially with the helium flow being reduced to 40 ml/min simultaneously. The flow rate of the mixture of CF_3OF and F_2 decreased slowly as the pressure dropped in the cylinder and was adjusted over time to maintain the flow at 10–30 ml/min during the addition. The flow of CF_3OF and F_2 from the bomb reactor continued for 2.5 h. The CO was then stopped after 5 min and the helium flow was continued for 45 min. The contents of the 196 °C trap were separated by trap-to-trap distillation using two traps at −135 and −196 °C, respectively. About 45.6 mmol CF_3OF contaminated with a little COF_2 was collected in −196 °C trap, and 12.4 mmol of the mixture of CF_3OF and $CF_3OC(=O)F$ were collected in −135 °C trap. The mixture in the −135 °C trap was then separated using −130 and −196 °C traps. Pure $CF_3OC(=O)F$ (1.8 mmol) was collected in the −130 °C trap. The isolated yield of $CF_3OC(=O)F$ was approximately 3%.

Acknowledgement

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