An *in situ* IR study of the thermal decomposition of trifluoroacetic acid

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The pyrolysis of trifluoroacetic acid has been carried out in the temperature range 513–593 K both as the neat gas and also in the presence of nitrogen as diluent. Reactions were carried out in a sealed sodium borosilicate glass cell, and the progress of the reaction was monitored by *in situ* Fourier transform IR spectroscopy. The principal products are CHF_3, CF_3COF and CO_2, but significant amounts of other species including C_2F_4, CO and SiF_4 are also produced. The formation of HF is observed directly for the first time for this reaction as is the formation of a number of other minor species (formaldehyde, formyl fluoride and hexafluoropropylene oxide).

Introduction

The decomposition of simple carboxylic acids may proceed *via* either dehydration or decarboxylation.[1] Dehydration is, however, not possible for trifluoroacetic acid and other perfluorinated acids but loss of HF is a reasonable alternative. The thermal decomposition of trifluoroacetic acid in a static system has been previously studied by Blake and Prichard[2] in which both silica and steel cells were used. Trifluoroacetic acid was decomposed neat for small percentage decompositions. Analysis of the reaction products was carried out primarily using *in situ* pressure measurements and *ex situ* gas chromatography on the reaction products. The proposed mechanism for the decomposition (Scheme 1) involves initial intramolecular loss of HF giving the diradical, $^{\bullet}CF_2CO_2{}^{\bullet}$, which may decompose to give either $:CF_2$ and CO_2 or to CF_2O and CO. The overall reaction mechanism is complex but leads to the formation of CO_2, CO, difluoromethyl trifluoroacetate and trifluoroacetyl fluoride as the major products.

$$CF_3CO_2H \longrightarrow HF + {}^{\bullet}CF_2CO_2{}^{\bullet} \qquad (1)$$

$${}^{\bullet}CF_2CO_2{}^{\bullet} \longrightarrow :CF_2 + CO_2 \qquad (2)$$

$${}^{\bullet}CF_2CO_2{}^{\bullet} \longrightarrow CF_2O + CO \qquad (3)$$

Scheme 1

The laser-induced, SF_6-sensitised decomposition of trifluoroacetic acid has also been studied[3] and proceeds by a similar mechanism. The photolytic decomposition of a gaseous mixture of silane and trifluoroacetic acid (using CO_2 laser radiation)[4] has been proposed to proceed by the insertion of silylene, $:SiH_2$, into the OH bond of trifluoroacetic acid, giving silyl trifluoroacetate. Subsequent decomposition gives the diradical, $^{\bullet}CF_2CO_2{}^{\bullet}$, leading to the formation of CO and CF_2O. A preliminary study of the pyrolysis of trifluoroacetic acid alone was also undertaken by Ashworth and Harrison,[5] which was carried out using a sealed steel cell and concentrated on heterogeneous reactions, finding no evidence for difluorocarbene formation in that system. This study, however, was carried out using a silica cell and focuses on the homogeneous reactions of the trifluoroacetic acid pyrolysis system.

Experimental

Trifluoroacetic acid, hexafluoropropylene oxide and bromine were all obtained from Aldrich and used as supplied, the former two compounds after checking the IR spectra against those of standard samples[6,7] to ensure their purity. Carbon dioxide was produced from the pyrolytic decomposition of dibenzoyl peroxide, rather than solid carbon dioxide, in order to avoid the introduction of water into the system, and then transferred to the reaction vessel.

The experiments were carried out in a grease-free sodium borosilicate glass cell. The cells were cylindrical, of 13.5 cm length and internal diameter 2.3 cm, with KBr windows fixed on with Crystal sealant.[5] IR spectra were recorded using a Nicolet 20SXC IR spectrometer. During the reaction time, the cell was heated by use of Thermolyne heating tape, controlled by an analogue temperature controller, fitted with a K-type thermocouple such that the temperature could be held steady to ±2 K. Each cell was conditioned prior to use by heating up to 673 K under a dynamic vacuum for 4 h and then decomposing trifluoroacetic acid several times.

The cell used was initially evacuated for *ca.* 30 min at ambient temperature before a background IR spectrum was taken. Known pressures of trifluoroacetic acid (at 0–20 mbar at STP) were then admitted to this IR cell at room temperature, and the cell temperature raised as quickly as possible to the desired reaction temperature before scanning of the IR spectrum was initiated. Where the reaction was carried out under nitrogen, the cell was first filled with the desired pressure of trifluoroacetic acid and then nitrogen was added from a vacuum line. Spectra were recorded at appropriate intervals throughout each run. Each run was then continued for the duration of three half-lives. Gas phase abundances of component species present were evaluated by peak integration of characteristic IR bands. Depending on the initial pressure of trifluoroacetic acid employed, the loss of acid was determined by use of the peak area for the OH stretch (3557 cm^{-1}) or the more intense C=O stretch (1819 cm^{-1})[6] (the trifluoroacetic acid is monomeric in the gas phase above *ca.* 430 K) shown in Fig. 1.

Hexafluoropropylene oxide (0–15 mbar) was heated in the IR cell, under nitrogen at 413–473 K to produce difluoromethylene, $:CF_2$. This experiment was repeated under an atmosphere of nitrogen (*ca.* 950 mbar) and carbon dioxide (*ca.* 50 mbar), to study the reaction between difluoromethylene and carbon dioxide.

Results

Trifluoroacetic acid, in the pressure range 0–20 mbar, was thermally decomposed over the temperature range 513–593 K. A large number of peaks are seen in the IR spectra taken and

Table 1 Assignment of IR peaks (4000–400 cm^{-1}) observed in trifluoroacetic acid pyrolysis

Observed peak, ν/cm^{-1}	Species	Reference peak, ν/cm^{-1}	Ref.
3962	HF	3962 (centroid)	8
3750	H_2O	3756	8
3660	H_2O	3657	8
3035	CHF_3	3036	21
2396–2234	CO_2	2349 (centroid)	8
2141	CO	2143 (centroid)	8
1943	CF_2O	1928	8
1894	CF_3COF	1895	22
1820	CF_3CO_2H	1819	6
1560	HFPO[a]	1555	7
1507	Solid product		
1458, 1443	Solid product		
1419	$(CHF_2)_2O$	1419	23
1375	HFPO	1375	7
1349	$(CHF_2)_2O$	1349	23
1338	C_2F_4	1337	24
1326	Unknown		
1282	HFPO, CF_4	1277, 1283	7, 25
1235	HFPO	1235	7
1207	CF_3COF	1214, 1202	22
1195	$(CHF_2)_2O$, CF_3OCHF_2	1197, 1196	23
1192	CF_3CO_2H	1185	6
1185	C_2F_4	1186	24
1161	HFPO	1166	7
1155	CHF_3	1152	21
1148	CHF_3	1149	21
1144	$(CHF_2)_2O$, CF_3OCHF_2	1146, 1148	23
1128	HFPO	1128	7
1107	CF_3COF	1106	22
1100	CF_3COF	1100	22
1092	CF_3COF	1092	22
1037	SiF_4	1031	8
720	HFPO	720	7
699	CF_3COF	699	22
692	CF_3COF	692	22
685	CF_3COF	685	22
669	CO_2	667	8
648	Unknown		
632	CF_4	633	25
617	CF_3COF	617	22
406	C_2F_4	406	24
392	SiF_4	392	8

[a] HFPO = hexafluoropropylene oxide.

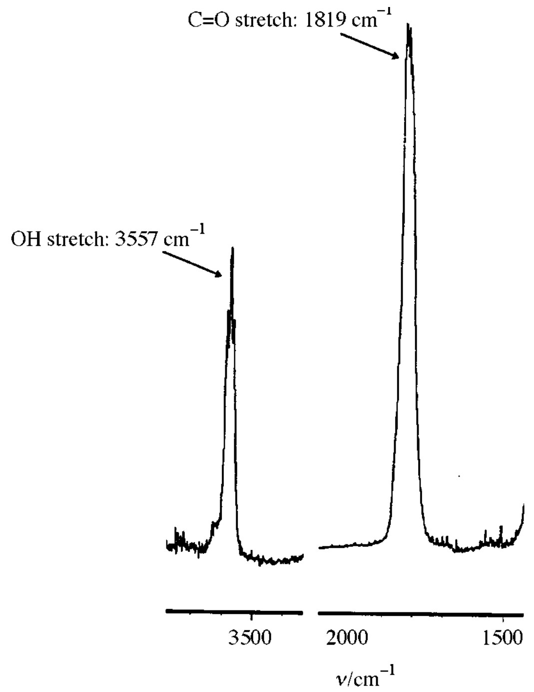


Fig. 1 IR bands used in monitoring trifluoroacetic acid loss

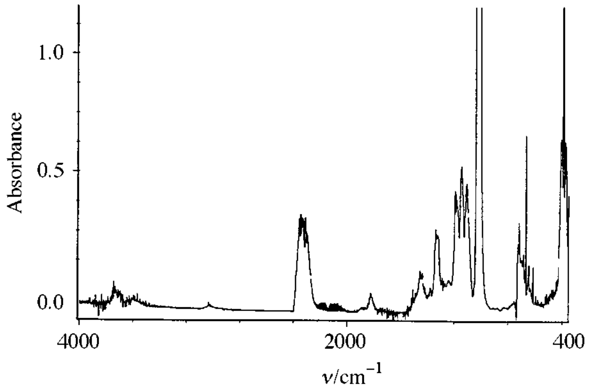


Fig. 2 IR spectrum of the reaction products from decomposition of trifluoroacetic acid at 543 K

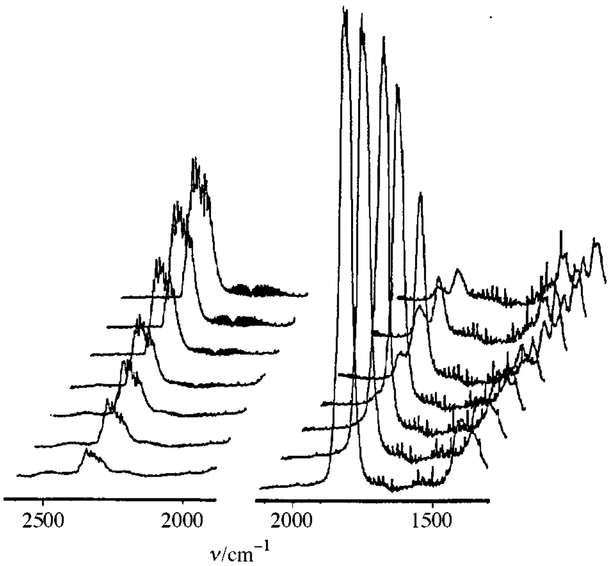


Fig. 3 Time-resolved spectra for the decomposition of trifluoroacetic acid at 543 K, illustrating the decay of the C=O band at 1819 cm^{-1} and the production of CO and CO_2

the majority may be readily assigned. The assignment of peaks in the CF_3 stretching region from *ca.* 1300–1100 cm^{-1} is difficult due to the large number of overlapping peaks. The same peaks are seen, irrespective of the temperature in this range at which the pyrolysis is carried out although the area of each peak does vary as a function of time elapsed, initial pressure of trifluoroacetic acid and temperature. A spectrum of the final reaction mixture is shown in Fig. 2 and assignments for the IR peaks observed are presented in Table 1.

The principal changes in the spectrum with time are the loss of the trifluoroacetic acid peaks (at 3557, 1820, 1415, 1251, 1206, 1185, 1116, 778, 663, 591, 574 and 507 cm^{-1}) as shown for the carbonyl stretch in Fig. 3, and the evolution of both CO_2 (2396–2234 and 669 cm^{-1}) and CO (centroid at 2141 cm^{-1}) as also shown in Fig. 3. Neither loss of trifluoroacetic acid, as shown in Figs. 4 and 5, nor production of carbon dioxide or carbon monoxide have constant reaction order.

CHF_3 is also evolved although it is difficult to quantify because of overlapping peaks due to other species for the weak C–H stretch at 3035 cm^{-1} and the stronger CF_3 stretch at 1155 and 1148 cm^{-1}.

The centroid of the HF vibrational P and R bands lies at 3962 cm^{-1}[8] with a rotational spacing of 41–37 cm^{-1}[9] (see Fig. 6). The P and R bands grow slowly but are not present in the final spectra due to the high reactivity of HF. The peaks lying at 4203 [R(6)], 4174 [R(5)], 4143 [R(4)], 4110 [R(3)], 4075 [R(2)],

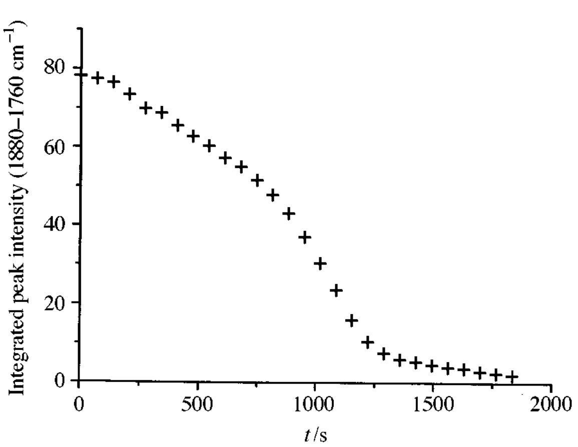


Fig. 4 Loss of trifluoroacetic acid at 553 K, monitored using the C=O band

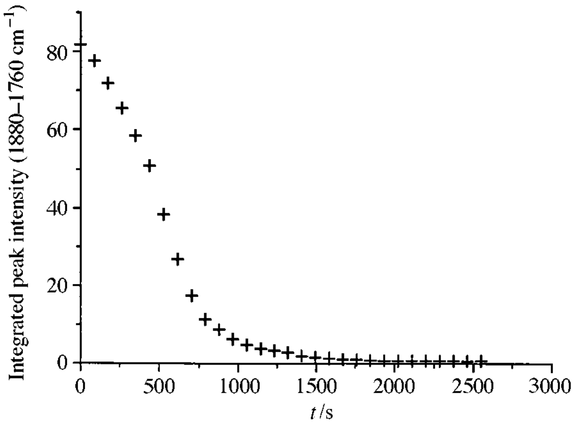


Fig. 5 Loss of trifluoroacetic acid at 563 K, monitored using the C=O band

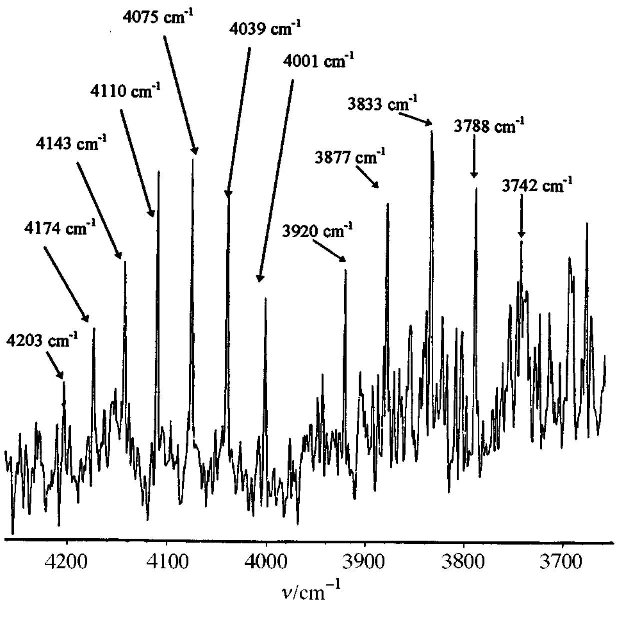


Fig. 6 IR spectrum of hydrogen fluoride produced during the decomposition of trifluoroacetic acid at 543 K

4039 [R(1)], 4001 [R(0)], 3920 [P(1)], 3877 [P(2)], 3833 [P(3)], 3788 [P(4)] and 3742 cm^{-1} [P(5)][10] are evidence of the existence of free HF in the static system.

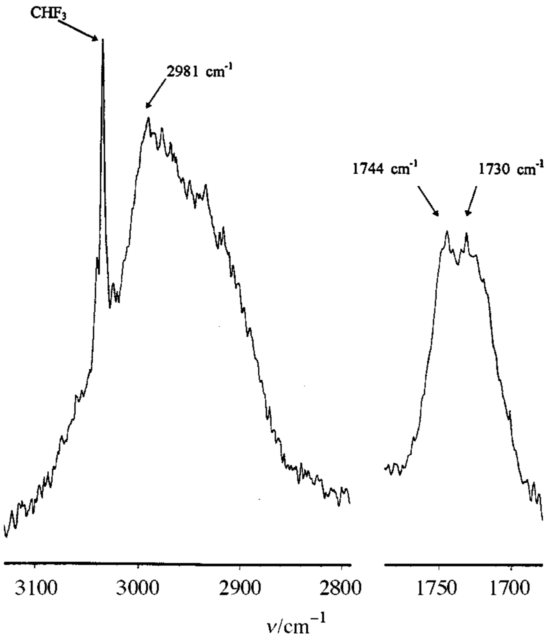


Fig. 7 IR spectra of formaldehyde and formyl fluoride produced during the decomposition of trifluoroacetic acid at 523 K

The presence of :CF_2 in the thermal decomposition of trifluoroacetic acid may be inferred from the scavenging reaction with either HCl or Br_2.[11] Pyrolysis of 7 mbar initial pressure of trifluoroacetic acid, with 300 mbar of Br_2 was carried out at 523 and 553 K. In each case CF_2Br_2 was formed, identifiable from the peak in the IR spectrum at 831 cm^{-1}[12] (the peak at 1153 cm^{-1} overlaps with the peak at 1149 cm^{-1} due to CHF_3).

The formation of C_2F_4, observed from the peaks at 1338, 1185 and 406 cm^{-1},[24] from the dimerisation of :CF_2 is also proof of the existence of :CF_2 in the reaction mixture. A number of minor products are also observed in the pyrolysis of trifluoroacetic acid. Hexafluoropropylene oxide is formed even though it readily decomposes to trifluoroacetyl fluoride and difluorocarbene at these temperatures, peaks being observed growing in for this species at 1560, 1375, 1282, 1235, 1161, 1128 and 720 cm^{-1} which then diminish in intensity. A peak grows in at 632 cm^{-1}[25] for CF_4, which is seen in small amounts.

At the lower temperatures employed in this study (<540 K), somewhat surprisingly, formaldehyde is also seen in small amounts, as indicated by the carbonyl peak at 1744 cm^{-1}, along with formyl fluoride, which is best seen from its C–H stretch at 2981 cm^{-1} (the intensities of the respective peaks are such that the carbonyl peak at 1837 cm^{-1}[13] cannot be seen as it is obscured by the remaining trifluoroacetic acid in all spectra taken) as shown in Fig. 7.

Alterations in temperature of the reaction produced a change in the rate of decomposition of trifluoroacetic acid, with an increase in temperature leading to an increase in decomposition rate, and gave the same products in slightly differing final ratios. The addition of nitrogen to the trifluoroacetic acid as a diluent did not affect the reaction.

Discussion

Although the major products from the decomposition of trifluoroacetic acid are carbon dioxide, carbon monoxide, trifluoroacetyl fluoride and trifluoromethane, as observed previously,[2–5] a number of species have been postulated in previous reaction schemes without any direct spectroscopic evidence,[2–5] most importantly HF and :CF_2. In addition, other species observed in this study which have not been observed previously in this system include hexafluoropropylene oxide, formaldehyde and formyl fluoride. From our observations, we suggest a revised reaction scheme for the pyrolytic decomposition of trifluoroacetic acid (Scheme 2). Reaction (4) is preferred to the sequential reactions (1) and (2) postulated in earlier work[2–4] as there is no evidence to suggest the existence of the diradical $^{\bullet}CF_2CO_2^{\bullet}$. The major fate of HF seems to be to react

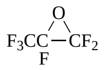
$$CF_3CO_2H \longrightarrow :CF_2 + HF + CO_2 \tag{4}$$

$$HF + :CF_2 \longrightarrow CF_3H \tag{5}$$

$$:CF_2 + CO_2 \longrightarrow CF_2O + CO \tag{6}$$

$$HF + CF_3CO_2H \longrightarrow CF_3COF + H_2O \tag{7}$$

$CF_3COF + :CF_2 \longrightarrow$



(8)

$$:CF_2 + CF_3COF \longrightarrow (CF_3)_2C{=}O \tag{9}$$

$$2{:}CF_2 \longrightarrow C_2F_4 \tag{10}$$

$$:CF_2 + CF_2O \longrightarrow CF_4 + CO \tag{11}$$

$$CF_2O + H_2O \longrightarrow CO_2 + 2HF \tag{12}$$

$$CF_2O + HF \longrightarrow CF_3OH \tag{13}$$

$$:CF_2 + H_2O \longrightarrow CHF_2OH \tag{14}$$

$$CHFO + H_2O \longrightarrow CH_2FOH \tag{15}$$

$$CHF_2OH \longrightarrow CHFO + HF \tag{16}$$

$$CH_2FOH \longrightarrow CH_2O + HF \tag{17}$$

$$CHFO \longrightarrow CO + HF \tag{18}$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O \tag{19}$$

$$2{:}CF_2 + SiO_2 \longrightarrow SiF_4 + 2CO \tag{20}$$

Scheme 2

either with the walls to form SiF_4 or with $:CF_2$ to form CHF_3 [reactions (5) and (19)].

CF_2O could not be observed directly in this work, although previously observed by IR both by Pola[3] and by Blake.[2] However, it is known to react quickly with water *via* the diol [$CF_2(OH)_2$] to give HF and CO_2,[14] and therefore might be expected not to be readily observed. One possible mechanism for the formation of CF_2O is *via* reaction between $:CF_2$ and CO_2 [reaction (6)] both of which have been shown to be present in the reaction mixture. However, copyrolysis of hexafluoropropylene oxide (HFPO) and CO_2 over a range of temperatures between 413 and 473 K does not yield any CO or CF_2O. Although hexafluoropropylene oxide is known as a difluoromethylene source,[15] it is not known whether thermal decomposition of hexafluoropropylene oxide and trifluoroacetic acid yields difluoromethylene in the same spin state, *i.e.* singlet or triplet. Therefore, although no CF_2O is formed from a reaction between $:CF_2$ pyrolytically formed from hexafluoropropylene oxide and carbon dioxide, it is possible for the reaction between $:CF_2$ pyrolytically formed from trifluoroacetic acid to react with carbon dioxide to give CF_2O as in reaction (6). In addition it seems likely that either the reaction of water and difluorocarbene [reactions (14), (16) and (18)] or the reaction of difluorocarbene with the silica in the cell walls is the most important route to formation of carbon monoxide.[16,17]

Difluoromethyl trifluoroacetate (identifiable from its C–H stretching band at 3100 cm^{-1} or its carbonyl stretch at 1836 cm^{-1}) was not observed as either an intermediate or final product in any of the reactions carried out, contrary to the results of Blake and Prichard.[2] Difluorocarbene is known to insert into O–H bonds[18] and its possible insertion into the O–H bond of trifluoroacetic acid occurs. However, the reverse reaction *via* a simple five-membered transition state, aided by hydrogen bonding between the difluoromethyl hydrogen and the carboxy oxygen is also possible (Fig. 8).

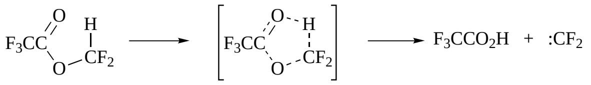


Fig. 8 Transition state for decomposition of trifluoromethyl difluoroacetate

The number of minor products observed in the trifluoroacetic acid system indicates that the mechanism is more complicated than at first thought by other authors.[2,3,5] Hexafluoropropylene oxide is formed in relatively large amounts by the insertion of $:CF_2$ into the carbonyl bond of trifluoroacetyl fluoride. Neither hexafluoroacetone nor its hydrate (1,1,1,3,3,3-hexafluoropropane-2,2-diol) are observed although it could be formed by the insertion of $:CF_2$ into the C(O)–F bond of trifluoroacetyl fluoride or by the fluoride-ion catalysed isomerisation of hexafluoropropylene oxide.[19] CF_4 is seen in small amounts which may be due to the reaction of $:CF_2$ with CF_2O [reaction (11)].[20]

The presence of amounts of formaldehyde as well as extremely small amounts of bis(difluoromethyl) ether and difluoromethyl trifluoromethyl ether is most likely to be due to the intermediacy of formyl fluoride, CHFO. This is formed by reaction (14), *via* the insertion of CF_2 into the OH bond of water to give difluoromethanol, CHF_2OH. This species can react either by the loss of HF to form a carbonyl or by insertion of $:CF_2$ into the OH bond to give an ether. These *gem*-hydroxy, fluoro species are highly reactive and, although raising the temperature will increase the concentration of $:CF_2$, it will also dramatically decrease the lifetime of these species, ensuring that these three minor products are present in much smaller quantities at higher temperatures, despite their individual high thermal stabilities.

Conclusions

The pyrolysis of trifluoroacetic acid has been carried out at a variety of temperatures, 513–593 K, both neat and diluted by nitrogen in a sodium borosilicate glass cell. The presence of nitrogen as a buffer gas does not affect the course of the reaction. The reaction proceeds, as found previously,[2] by initial loss of hydrogen fluoride, leading to formation of difluoromethylene and carbon dioxide. The reaction is complex and does not proceed with any simple or constant reaction order for loss of trifluoroacetic acid or formation of products. The fate of the majority of the hydrogen fluoride and difluoromethylene formed is to react together to form CHF_3 but both are sufficiently reactive that several other reaction pathways also occur. The presence of difluoromethylene is verified by the formation of C_2F_4 (no cyclo-C_3F_6 is formed due to the low pressures employed). The presence of hydrogen fluoride is directly observed in this reaction for the first time. The formation of small amounts of CF_4 suggests the presence of CF_2O in the reaction mixture. The complexity of the decomposition is also illustrated by the formation of formyl fluoride, formaldehyde and hexafluoropropylene oxide as side products in varying ratios.

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