

ARRHENIUS PARAMETERS FOR THE THERMAL DECOMPOSITION OF FC(O)OOC(O)F

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Dedicated to the memory of the late Prof. Hans J. Schumacher
on the occasion of his 100th birthday

Abstract

The gas phase thermal decomposition of FC(O)OOC(O)F was studied at temperatures between 40 and 70 °C using FTIR spectroscopy to follow the course of the reaction. The decomposition was studied at different partial pressures of NO between 90 to 180 mbar and using N₂ to set the total pressure to 1000 mbar. The rate constant fits the Arrhenius equations

$$k_{\text{exp}}[\text{FC(O)OOC(O)F}] = (1.0 \pm 0.1) \times 10^{13} \text{ s}^{-1} \exp\left[-\frac{(23.9 \pm 0.9) \text{ kcal mol}^{-1}}{RT}\right] \text{ from which the}$$

O—O bond energy of (23.9 ± 0.9) kcal mol⁻¹ was obtained.

Resumen

La descomposición térmica del FC(O)OOC(O)F fue estudiada entre 40 y 70 °C por medio de espectroscopía FTIR para seguir el curso de la reacción. La descomposición se estudió a diferentes presiones de NO (90 a 180 mbar) agregando N₂ para dar una presión final de 1000 mbar. La constante de descomposición se ajusta a la ecuación

$$k_{\text{exp}}[\text{FC(O)OOC(O)F}] = (1,0 \pm 0,1) \times 10^{13} \text{ s}^{-1} \exp\left[-\frac{(23,9 \pm 0,9) \text{ kcal mol}^{-1}}{RT}\right]$$

a partir de la cual se determina la energía de enlace O—O como (23,9 ± 0,9) kcal mol⁻¹.

Introduction

Since the first synthesis of FC(O)OOC(O)F by Schumacher et al.[1] more than forty five years ago, much work has been done with this and other related halogen containing molecules. The ideas prevailing in the sixties, and particularly in Schumacher's group, were at the time

logically away from the urgencies of today's atmospheric sciences, though they were involved in countless projects dealing with halogenated molecules that later proved to have substantial impact on the chemistry of the terrestrial atmosphere [2-4]. After the recognition of the deleterious effect that the chlorofluorocarbons (CFCs) had on the ozone layer [5,6] and their replacement by hydrofluorocarbons, (HFCs) there have been exhaustive studies of the mechanisms, intermediates and final products involved in many of these halogenated molecules. In the last decade much work has been devoted to the study of the properties and reactions of many compounds and radicals containing only F, C and O atoms that can be formed in the laboratory as a result of the degradation of HFCs in the presence of oxygen and high concentrations of CO. The study of these reactions afforded many new compounds to be synthesized and used as precursors of atmospherically relevant radicals which were thus isolated [7-9]. One of such compounds is precisely FC(O)OOC(O)F that besides having being synthesized in more than one way [1,10-12], was used as a polymerization initiator [13]. Further studies on this peroxide over four decades involved the elucidation of its IR spectrum [14,15], studies of its gas phase structure [16], its chemistry [17] and its potential as reagent for synthesis [18,19]; a theoretical density functional study [20] and its involvement in atmospheric chemistry as a precursor of FCO₂ radicals that were isolated in low temperature matrices [21] and studied in their reactions with other atmospheric gas traces [22].

Kinetic data on thermal decomposition are needed in order to have reliable estimates of bond energies and to help in the elucidation of mechanisms and in the calculation of thermodynamic properties. Nevertheless, for fluorocarbonoxygenated peroxides and trioxides this kind of studies have been reported for just a few compounds like CF₃OOCF₃ [23], CF₃OOOCF₃ [24], CF₃OC(O)OOC(O)OCF₃ [25], CF₃OC(O)OOC(O)F and CF₃OC(O)OOCF₃ [26]. For the title compound, Schumacher's group gave a value of the O-O bond energy, derived from indirect studies [13]. In the present work the thermal decomposition rate constants for FC(O)OOC(O)F have been measured as a function of temperature and in the first order region providing a direct determination of the bond energy. The Arrhenius parameters obtained are discussed in comparison to the former bond energy determination and conform a contribution to the available atmospheric databases.

Results

The thermal decomposition of FC(O)OOC(O)F in presence of NO was evaluated at temperatures between 40 and 70 °C, using N₂ to set a total pressure of 1000 mbar. The disappearance of the reagent was followed using its absorption band at 1185 cm⁻¹ without need of subtraction from interfering products. The data were analyzed according to first-order kinetics:

$$-\frac{d[\text{FC(O)OOC(O)F}]}{dt} = k_{\text{exp}}[\text{FC(O)OOC(O)F}] \quad (1)$$

The first step in the decomposition of FC(O)OOC(O)F is the formation of FCO₂ radicals, which have a half-life long enough to recombine to give back the peroxide. A way to obtain the correct values for the kinetic parameters of the decomposition reaction is the rapid reaction of FCO₂ radicals by the addition of an effective scavenger. We studied the decomposition reaction of FC(O)OOC(O)F in presence of NO because it is well known that it reacts efficiently with

FCO_2 radicals [27]. The partial pressure of NO was varied between 90 and 180 mbar at each temperature of decomposition.

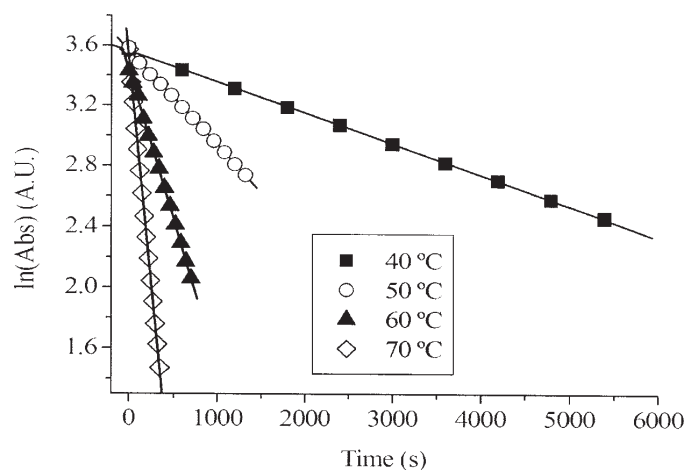


Figure 1: First-order kinetic curves at selected temperatures for the decomposition of $FC(O)OOC(O)F$.

Figure 1 shows plotting of the logarithms of absorbance vs. time for reactant loss with 120 mbar of NO. Good straight lines (not shown in the figure) were obtained for all NO pressures. At each temperature studied, the first-order rate constant was calculated by a least-squares method. Average rate constants are given in Table 1.

Table 1. First-order rate constants from decomposition of $FC(O)OOC(O)F$ in NO at different temperatures

First-order rate constants k (s^{-1})				
Temperature ($^{\circ}C$)	NO Partial Pressure (mbar)			
	90	120	150	180
40	1.89×10^{-4}	2.05×10^{-4}	2.12×10^{-4}	2.26×10^{-4}
50	6.06×10^{-4}	6.30×10^{-4}	5.82×10^{-4}	6.84×10^{-4}
60	1.82×10^{-3}	1.97×10^{-3}	1.86×10^{-3}	1.96×10^{-3}
70	5.68×10^{-3}	5.86×10^{-3}	6.15×10^{-3}	6.06×10^{-3}

To evaluate the Arrhenius parameters, the determined rate constants were used to construct an Arrhenius plot for every NO partial pressure, obtaining very good straight lines from the linear least-squares analysis in each case. Nevertheless, since the differences in the Arrhenius parameters for the different partial pressures of NO are within the experimental uncertainties, the Arrhenius equation for the decomposition was fitted to all the experimental points as can be seen in Figure 2. In this manner, only one averaged value was determined as:

$$k_{\text{exp}}[\text{FC(O)OOC(O)F}] = (1.0 \pm 0.1) \times 10^{13} \text{ s}^{-1} \exp\left[-\frac{(23.9 \pm 0.9) \text{ kcal mol}^{-1}}{RT}\right] \quad (2)$$

Figure 3 shows the IR spectra of reactants and/or products at different times of reaction. It can be seen that the decomposition results in the formation of CO_2 (2300 cm^{-1}), HF ($3830\text{--}4140 \text{ cm}^{-1}$), NO_2 (1600 cm^{-1}) and SiF_4 (1022 cm^{-1}). In some experiments FNO (1843 cm^{-1}) was detected as a transient species.

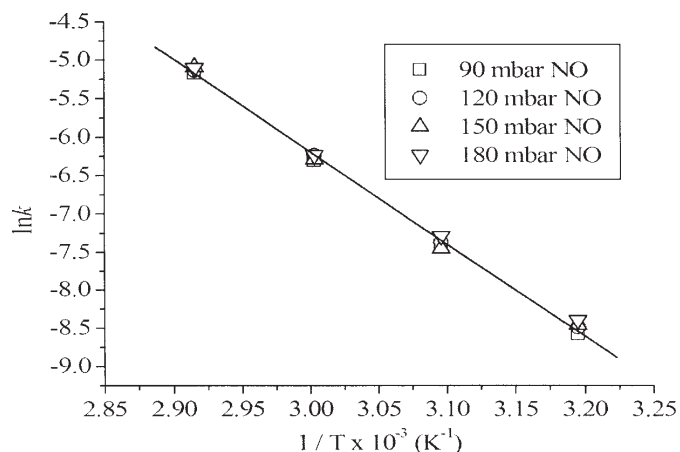


Figure 2: Arrhenius plot for the decomposition of FC(O)OOC(O)F .

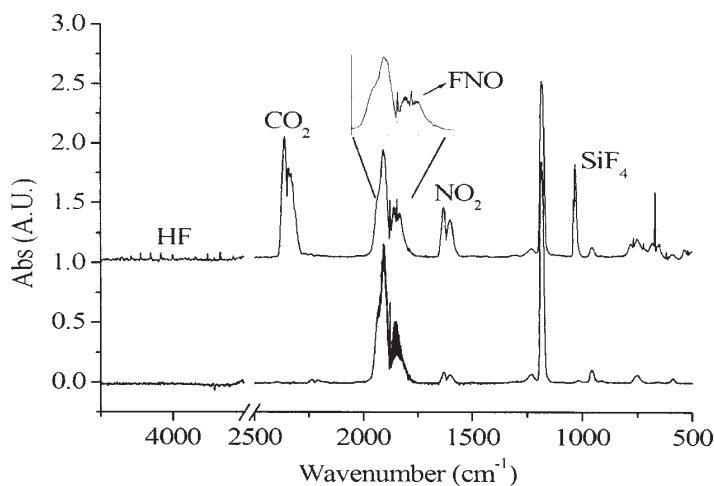


Figure 3: IR spectra of the reactants (lower trace) and products obtained (upper trace) in the decomposition of FC(O)OOC(O)F .

Discussion

The first step in the decomposition process of FC(O)OOC(O)F should be the breaking of the peroxide bond, the weakest bond in the molecule. The O—O rupture produces two FCO_2 radicals



In presence of NO, these FCO₂ radicals will react to form FNO and CO₂



Slightly differing values ($3.6\text{--}3.9 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) of the rate coefficient for this reaction have been measured [27-29] at room temperature. Comparing these values with the rate coefficient for the recombination of FCO₂ radicals to give the peroxide back, $7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, it is clear that the back reaction (-3) is absolutely suppressed [28-30].

The FNO was detected as a transient product in some experiments. After its formation via reaction (4), heterogeneous reactions with the walls of the reaction cell could have been responsible of the NO₂ formation, as well as of the appearance of HF and SiF₄.

Arvia et al. [11] studied the reaction of FC(O)OOC(O)F with NO at room temperature, they explained their results in terms of the overall reaction



Though there was no detailed indication of the amount of NO, the authors indicate that the reaction between the peroxide and NO was carried out in excess NO. As stated before, we found NO₂ and CO₂ as reaction products, but we did not observe the formation of CF₂O. In our experiments the partial pressure for the peroxide was 1.5-2.2 mbar and always at least 90 mbar of NO were added. Under these experimental conditions all the FCO₂ radicals should have reacted with NO through reaction (4).

FC(O)OOC(O)F decomposition in the presence of NO was studied at total pressures of 1000 mbar set with N₂. It is assumed that under these conditions the reaction runs in the high pressure region, as expected for a molecule of this complexity. Examples of similar peroxide species that achieve their first-order values at pressures higher than 500 mbar are (CF₃OC(O)O)₂ [25], (CH₃C(O)O)₂ [31], CF₃OOOCF₃ [24] and CH₃C(O)OONO₂ [32].

The derived activation energy is 23.9 kcal/mol and the extrapolated A factor is 1.0×10^{13} . The A factor obtained can be compared with those collected in Table 2. It can be seen that it is the lowest of the peroxides listed, and therefore indications pointing to some complex mechanism could be advanced. Nevertheless, we do believe the decomposition directly provides two smaller fragments in a simple bond fission. This hypothesis has been certified through the isolation of the FCO₂ radicals in low temperature matrices [21], prepared from pyrolysis of FC(O)OOC(O)F. Therefore, the difference in A factors should be rationalized in other terms. Also for comparison it is included in the Table the trioxide CF₃OC(O)OOOC(O)OCF₃ for which an even lower A factor has been reported. The pyrolysis of this molecule afforded, again in a simple direct decomposition reaction, the primary radicals that were subsequently trapped in low temperature matrices [8]. Therefore, simple direct O-O bond rupture can occur with A factors usually encountered for more complex reactions.

In terms of the π stabilization afforded by the two fragments formed, it can be seen from the Table that the hydrogenated peroxides have almost the same A factor (ranging from $10^{14.2}$ to $10^{14.4}$) as the fluorinated peroxide CF₃OC(O)OOC(O)OCF₃ (with an A factor of $10^{14.5}$). All these peroxides form two equal, bulky and delocalized acyloxy-radicals when decomposed. When a

Table 2. Pre-exponential factors and entropy of activation for selected peroxides.

Molecule	A-factor	ΔS^\ddagger (e.u.)	Ea	Reference
CF ₃ OC(O)OOC(O)F	10 ^{15.6}	10.5	29.4	[26]
CF ₃ OC(O)OOCF ₃	10 ^{13.9}	2.0	34.0	[26]
FC(O)OOC(O)F	10 ^{13.0}	-1.2	23.9	This work
CF ₃ OC(O)OOC(O)OCF ₃	10 ^{14.5}	5.5	28.2	[25]
CF ₃ OC(O)OOOC(O)OCF ₃	10 ^{12.9}	1.0	20.7	[34]
CH ₃ C(O)OOC(O)CH ₃	10 ^{14.2}	3.7	29.5	[31]
C ₂ H ₅ C(O)OOC(O)C ₂ H ₅	10 ^{14.4}	4.5	30.0	[35]
C ₃ H ₇ C(O)OOC(O)C ₃ H ₇	10 ^{14.3}	4.0	29.6	[35]

smaller fragment takes part in the molecule there is no simple correlation within the A factors. In the case of CF₃OC(O)OOC(O)F, again two contributions to π stabilization are possible (one through the FCO₂ radical [21] and the other through CF₃OCO₂) and the A factor is the highest.

The distinct feature shown in the Table is the activation entropy. FC(O)OOC(O)F is the only peroxide having a negative value. This could be interpreted not only in terms of forming two smaller fragments in the dissociation but also in acquiring the proper orientations for the leaving fragments during the decomposition.

A general overview of the bond energy for the peroxides shows that it increases when the peroxydic bond is directly attached to a non-carbonylic group having large electron withdrawing capacity.

The bond energy for FC(O)OOC(O)F has been the subject of four independent determinations. Arvia et al. [13] have informed a value of 31 ± 3 kcal mol⁻¹ though their determination was not a direct one. Years later, McKee et al. [20] performed a theoretical calculation using the most refined numerical tools available at that time. Their value of 14.8 kcal mol⁻¹ is far away from the numbers in Table 2 as is also the value of Cobos et al. [33] of 30.9 kcal mol⁻¹ that was derived theoretically from isodesmic reactions. Our value is the only one that comes from a direct determination and falls around the middle. A lower value for the dissociation energy than the more frequent 30 kcal mol⁻¹ seems reasonable in the light of the stability of the radicals formed, since FCO₂ radicals are very stable and long lived. Also reasonable seems the 34 kcal mol⁻¹ for the peroxide CF₃OC(O)OOCF₃ that does not have one of the two C(O) blocking units that protect the withdrawing of non-bonding electrons from the peroxidic bond.

The theoretical value of 14.8 kcal mol⁻¹ calculated at the B3LYP/6-31+G(d) level of theory by McKee et al. is unreasonable low in terms of the stability of the peroxide; since with this number as activation energy and the pre-exponential factor measured in this work, the half-life for the thermal decomposition at room temperature should be around 1 ms. The problems associated with the calculation of bond fission energies as the direct difference of the energy of products and reactants for the dissociation reaction are well known and Cobos et al. have discussed the case for FC(O)OOC(O)F in Ref 33. The theoretical value of 30.9 kcal mol⁻¹

obtained by Cobos et al. from isodesmic reactions is higher than ours in around seven kcal mol⁻¹. The use of isodesmic reactions is a very useful method for the evaluation of heats of formation with relative errors between 2-5%. Assuming the errors for the heats of formation of $FC(O)OOC(O)F$ and FCO_2 as ± 4 and ± 2 kcal mol⁻¹ respectively, the energy for the O-O bond fission reaction would give 31 ± 5 . A comparison with our value of 23.9 kcal mol⁻¹ still gives a difference beyond the error limits, but the discrepancy is rather small.

Experimental Section

All volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (Bell and Howell and MKS Baratron 220) and three U-traps connected via glass valves with PTFE stopcocks (Young, London). The vacuum line was connected to a photo-reactor, a thermal reactor and to a double-walled IR gas cell (optical path length 20 cm, Si windows 0.5 mm thick) placed in the sample compartment of an FTIR spectrometer (Bruker IFS28). This arrangement made it possible to follow either the course of the synthesis, the purification processes or the thermal decay of substances.

The synthesis of the $FC(O)OOC(O)F$ was carried out following the original Schumacher's recipe [1], which is the best method so far.

The thermal decomposition of $FC(O)OOC(O)F$ was studied using a double-walled IR cell in the sample compartment of the spectrometer. The outer jacket of the cell was connected to a thermostat, from which hot salty water flowed at temperatures ranging between 40 and 70 °C with an uncertainty of ± 0.1 °C. Once the cell reached the intended temperature, 90-180 mbar NO were admitted and then a diluted mixture of peroxide in N_2 was introduced. This procedure ensures the mixing of the reactants in a short time. The partial pressures of the peroxide in the cell ranged between 1.5 - 2 mbar and the total pressure was 1000 mbar. After the reaction was started a series of in-situ timely spaced IR spectra were obtained. The data processing of the kinetic measurements was done integrating the absorption band at 1185 cm⁻¹ which corresponds to the strongest band of the peroxide. In this manner it is possible to follow the disappearance of the peroxide without looking to the possible heterogeneous reactions of the FCO_2 radicals that very probably occurred in Schumacher's experiments since they could only look at the total pressure modification.

The products obtained (CO_2 , FNO, SiF_4 and HF) were identified from reference spectra of pure samples.

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