New Route to the Synthesis of Difluorodioxirane from FC(O)OF

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Introduction

Fluoroformyl hypofluorite has long been considered an unstable molecule[1] because the impurities present in the products during synthesis were responsible for its decomposition.[2] Even though FC(O)OF is well-characterized spectroscopically,[3] its photochemical study deserves special interest. Studies on infrared multiphoton (IRMP) excitation using a pulsed CO_2 laser have been undertaken in this paper. The results obtained show that the main reaction path goes through a heterogeneous reaction whose ultimate fate is the catalytic isomerization of FC(O)OF to F_2CO_2, a stable isomer proposed as an intermediate in the probable formation of O_3 by CF_2 in the stratosphere.[4]

Difluorodioxirane is the only known dioxirane that may be isolated as a pure substance and that may be thermally stabilized in the gas phase at room temperature. Its stability has allowed detailed high-resolution vibrational−rotational spectroscopic diffraction studies as well as electron diffraction studies.[5,6] Nevertheless, the synthetic method reported up to now required the reaction of FC(O)OF in the presence of CsF as the catalyst under specific conditions[7] and required either ClF, F_2, or Cl_2 to be added. The reaction mechanism involves an electron-transfer reaction where the presence of the halogen or interhalogen (or ClF) is essential for the F_2CO_2 formation.

In our study, we observed that the isomerization of the FC(O)OF is produced by the surface alkaline fluorides that were formed during the irradiation period while hypofluorite was being decomposed (thus eliminating the need for other catalysts). Under these conditions, the yield of isomer obtained is fairly high (60−75%). The formation of other minor products that were separated by distillation was also observed. The reactant and all the products were determined by IR spectroscopy.

Experimental Section

Caution! Fluoroformyl hypofluorite is potentially explosive, especially in the presence of oxidizable materials. It should be handled with proper safety precautions and only in millimolar quantities.

Materials and Apparatus. A sample of FC(O)OF was synthesized according to Argüello et al.[2] and distilled in a bath at −120 °C. The gases were manipulated in a hydrocarbon-free Pyrex glass vacuum line with a turbomolecular pump that reached a residual pressure lower than 10^{-8} Torr, as measured with a high vacuum manometer.

A pulsed, tunable TEA−CO_2 laser, designed and built in this laboratory,[8] was used. The main emission bands are centered at 9.4 and 10.6 μm. The irradiation wavelength was selected with a spectrum analyzer (CO_2 laser spectrum analyzer). Pyroelectric detectors, GENTEC 500, were used to measure the incident energy of the laser pulse before and after irradiation, averaging various pulses in each case.

Quantification of the consumed reactant and of the products formed was performed by IR spectroscopy using a System 2000, Perkins-Elmer FTIR with 1 cm^{-1} resolution. The corresponding calibration curves were recorded for all of the pure species.

Many different reaction cells were tested by using Pyrex glass and stainless steel cylindrical bodies and exchanging different types of windows (NaCl, KCl, and BaF_2) to close both ends. Thermal and irradiation experiments were performed; in some of them, Na_2SiF_6, obtained commercially and properly dried, was added; and the experiments were carried out at different reagent pressures. The irradiation geometry was focalized at the center of the cell.

Results and Discussion

The results obtained from the irradiation of a sample of FC(O)OF in a Pyrex cell with NaCl windows at relatively high fluences (>16 J/cm^2) showed decomposition and a white deposit on the windows. This fact prompted us to perform experiments using combinations of different cells and windows (see Table 1).

All cells were passivated with $(FC(O)O)_2$ until a decomposition no higher than 1% was found. Once these requirements were fulfilled, the IRMP irradiation experiments were performed as follows: the IR spectrum of the empty cell was first obtained and then about 4 Torr of total pressure of FC(O)OF was loaded into the cell, and another IR spectrum was taken. The sample was irradiated with 3000 pulses of the CO_2 laser tuned to the 10R32 emission line (983.29 cm^{-1}), resonant with one of the absorption bands of the fluoroformyl hypofluorite (ν_3 (a′))[4] at a fluence of 19 J/cm^2, without interference from the reaction products. After being irradiated, a new IR spectrum was taken; a new sample of FC(O)OF was loaded; and without irradiation, it was observed whether or not spontaneous reaction occurred by taking sequenced IR spectra every 5 min.

The experimental results obtained with the foregoing procedure are shown in Table 1. In the case of the Pyrex NaCl and Pyrex KCl cells, the following is observed. After passivation, the IR spectra of the empty cells show a band at 720 and 735 cm^{-1}, respectively, corresponding to a compound deposited on the surface of the windows. The compound is strongly adsorbed into the windows, since it remains after evacuation. When the IRMP irradiation of the hypofluorite sample begins, the formation of a new white deposit on the windows is evident to the naked eye; nevertheless, the IR spectrum shows essentially the bands corresponding to FC(O)F and sodium or potassium

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(1) Cauble, R. L.; Cady, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 5161.
(2) Argüello, G. A.; Balzer-Jöllenbeck, G.; Jülicher, B.; Willner, H. *Inorg. Chem.* **1995**, *34*, 603.
(3) Argüello, G. A.; Jülicher, B.; Ulic, S. E.; Willner, H.; Casper, B.; Mack, H. G.; Oberhammer, H. *Inorg. Chem.* **1995**, *34*, 2089.
(4) Argüello, G. A.; Jülicher, B.; Willner, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1108.
(5) Casper, B.; Christen, D.; Mack, H. G.; Oberhammer, H.; Argüello, G. A.; Jülicher, B.; Kronberg, M.; Willner, H. *J. Phys. Chem.* **1996**, *100*, 3983.
(6) Bürger, G.; Weinrath, P.; Argüello, G. A.; Jülicher, B.; Willner, H.; DesMarteau, D. D.; Russo, A. *J. Mol. Spectrosc.* **1994**, *168*, 607.
(7) Russo, A.; DesMarteau, D. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 905.
(8) Azcárate, M. L. Ph.D. Thesis, University of Buenos Aires, Buenos Aires, 1986.

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Table 1. Isomerization and Decomposition of FC(O)OF in Pyrex Cells with Different Windows

	passivation with $(FC(O)O)_2$		
sequence	NaCl	KCl	BaF_2
IR bands after passivation	band at 720 cm^{-1}	band at 735 cm^{-1}	no bands
decomp after 1 h	1% decomp	1% decomp	1% decomp
prod after irradiation	FC(O)F, $CF_3OOC(O)F$	FC(O)F, $CF_3OOC(O)F$	$(FC(O)O)_2$
deposit after evacuation	observed	observed	not observed
reaction after new loading	100% conversion 65% CF_2O_2	100% conversion 75% CF_2O_2	1% conversion

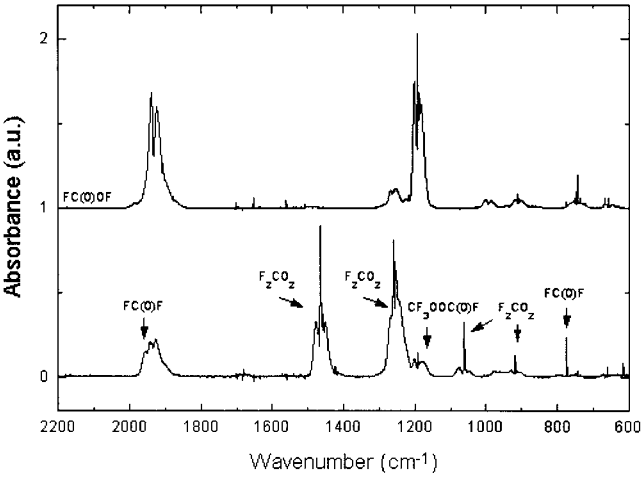

Figure 1. Sequence of IR spectra for the spontaneous reaction of FC(O)OF in the Pyrex NaCl cell. Upper trace: 4 Torr of total pressure of pure FC(O)OF at $t = 0$. Lower trace: 15 min later.

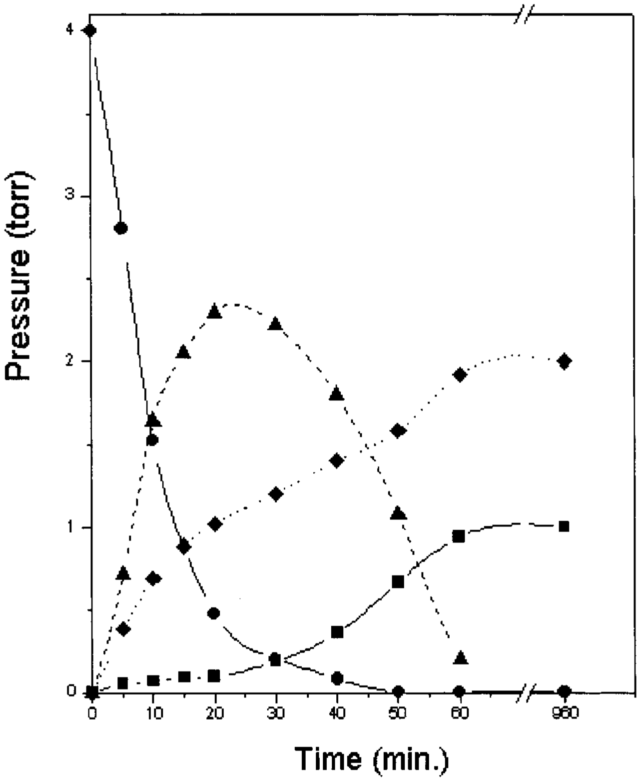

Figure 2. Time variation in the pressure of FC(O)OF (●) and the products FC(O)F (◆), F_2CO_2 (▲), and $CF_3OOC(O)F$ (■) in the spontaneous reaction in the Pyrex NaCl cell.

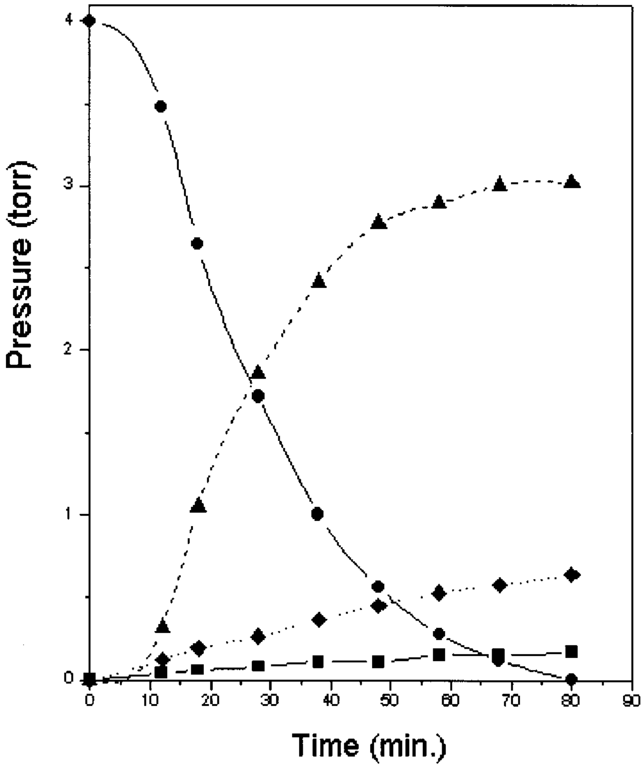

Figure 3. Time variation in the pressure of FC(O)OF (●) and the products FC(O)F (◆), F_2CO_2 (▲), and $CF_3OOC(O)F$ (■) in the spontaneous reaction in the Pyrex KCl cell.

hexafluorosilicate, depending on the window used, without any further indication of the new substance deposited. After evacuation of the cell, the IR bands at 720 (735) cm^{-1}, corresponding to $Na_2(K_2)SiF_6$, can still be observed, and from this moment on, their intensity remains the same.

Loading of a new sample of FC(O)OF shows the spontaneous reaction of hypofluorite in both cells. In the Pyrex NaCl cell, the conversion reaches 100% at 50 min; FC(O)F, $CF_3OOC(O)F$,[9−11] and F_2CO_2 (difluorodioxirane), the wanted isomer of hypofluorite,[5,6] are formed. In the Pyrex KCl cell, 100% decomposition is reached more slowly, and the same products, although in different yields, are formed.

Similar experiments using progressively higher pressures of reactant were carried out up to a maximum of 400 Torr of FC(O)OF loaded into the cell. This limit was self-imposed in order to avoid using quantities bigger than 2 mmol. Besides, at these pressures, it is rather difficult to follow the time variation in the concentration of difluorodioxirane since the absorptions are extremely high. Nevertheless, good conversion yields were still observed, though a declining trend was detected.

The infrared spectra corresponding to a typical run for the spontaneous reaction of FC(O)OF in the Pyrex NaCl cell are shown in Figure 1. The experiment shown corresponds to a low pressure run to portray a clear temporal variation of the species involved. The upper trace shows the bands corresponding to the reactant just after the cell has been loaded, and the lower

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(9) Talbott, R. L. *J. Org. Chem.* **1968**, *33*, 2095.
(10) Cauble, R. L.; Cady, G. H. *J. Org. Chem.* **1968**, *33*, 2099.
(11) Pilipovich, D.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1972**, *11*, 2531.

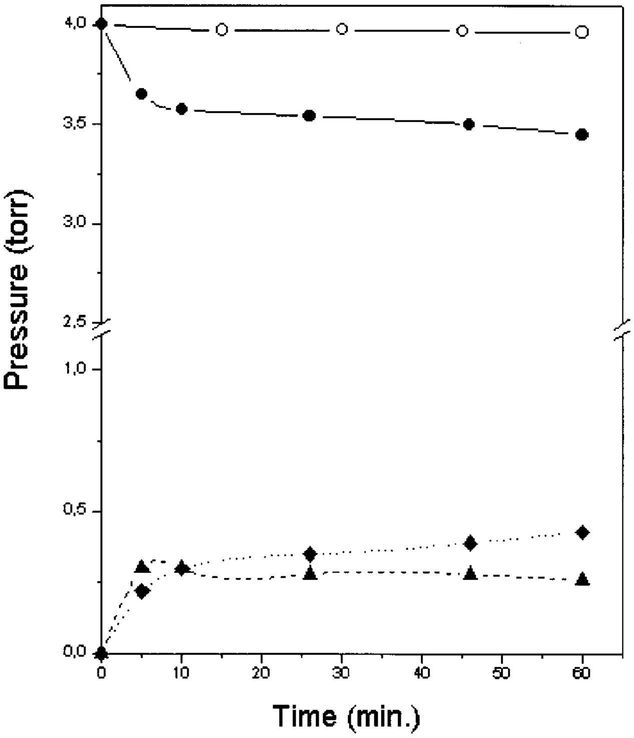

Figure 4. Time variation of the pressure in the spontaneous reaction of FC(O)OF in the Pyrex BaF_2 cell (○). The solid symbols represent FC(O)OF (●), FC(O)F (◆), and F_2CO_2 (▲) in the stainless steel BaF_2 cell with added Na_2SiF_6.

trace shows the total spectrum of the products 15 min later, where it is clearly seen that, besides some FC(O)F, the major product is difluorodioxirane, F_2CO_2.[7]

The time variation in the concentration decrease of the reactant and the concentration increase of the products is shown in Figure 2 for the Pyrex NaCl cell and in Figure 3 for the Pyrex KCl cell. The former cell shows a 100% conversion of the reactant at 50 min. During this period, difluorodioxirane reaches its maximum concentration at 20 min with 60% yield and later decomposes into FC(O)F and $CF_3OOC(O)F$. Even though the same products are observed in the Pyrex KCl cell, the 100% FC(O)OF conversion occurs with a 75% yield of difluorodioxirane at 80 min. Instead, a lower decomposition was observed than in the Pyrex NaCl system.

Because of these results, it could be thought that the catalyst could be $Na_2(K_2)SiF_6$ or Na(K)F formed by the attack on the windows of the flourine atoms coming from the FC(O)OF decomposition. The reactions have been known[12] for a long time and have been discussed extensively. To determine if the alkaline compounds are the catalysts, similar experiments were carried out in a Pyrex cell with BaF_2 windows, which should not be attacked by the fluorine atoms because this setup, after proper surface conditioning, should be inert for fluorocarbooxygenated compounds. At variance with the observations in the previous cells, it is seen in Table 1 that there is no formation of the deposit on the windows. The irradiation product obtained is $(FC(O)O)_2$. The loading of a new sample to observe its spontaneous reaction shows a 1% decomposition at 1 h, similar to that observed before irradiation. This observation is presented in Figure 4. These results indicate that when no sodium or potassium is available to form alkaline compounds, there is no catalytic activity, and the homogenous recombination reaction of the FCOO radicals takes place to give bisfluoroformylperoxide, $(FC(O)O)_2$.[13]

The next step required was to put commercial $Na_2(K_2)SiF_6$ in an inert cell. Therefore, experiments in a stainless steel cell with BaF_2 windows in the presence of Na_2SiF_6 were carried out. After the cell conditioning was achieved, irradiation experiments were performed with the added salt lying on the surface of the bottom window in the otherwise evacuated cell. At the end of the irradiation, the formation of SiF_4 was observed in addition to the white deposit on the windows. It is known that Na_2SiF_6 decomposes around 600 °C in SiF_4 and NaF;[14,15] these temperatures are easily obtained on the surface of the windows because of the discharge of the CO_2 laser.

Irradiation experiments were then performed by loading into the cell 4 Torr of total pressure of FC(O)OF, and the formation of FC(O)F, CO, CO_2, and SiF_4 was observed. After the irradiation, a new sample was loaded to observe if a spontaneous reaction of hypofluorite took place. The products F_2CO_2 and CF_2O were formed, as shown in Figure 4. The isomerization percentage obtained in this cell is only 6%, well below that obtained in the Pyrex NaCl and Pyrex KCl cells. This result indicates that the $Na_2(K_2)SiF_6$ is not the catalyst; neither is the NaF formed by the thermal decomposition of the Na_2SiF_6 that was added. Therefore, the compound that has truly catalytic activity should be the Na(K)F, which would form while the FC(O)OF is irradiated (that is, the Na(K)F that stays strongly stuck at the Na(K)Cl window). As known, this compound is transparent in the IR region, so the cells were dismantled at the end to analyze the deposits stuck to the windows. IR spectra still showed the presence of hexafluorosilicates, and an X-ray diffraction study confirmed the presence of those compounds and also proved the presence of alkaline fluorides. Therefore, the formation of the deposits is attributed on one hand to the known reaction of SiF_4 (in our case, formed during the surface conditioning of the cells and during the irradiation period) with NaCl or KCl to give sodium or potassium hexafluorosilicates,[16,17] which after irradiation are partly converted to NaF or KF (IR-transparent compounds that remain undetected in our usual experiments). On the other hand, the formation of the deposits is attributed to the direct formation of NaF or KF in a reaction driven by the fluorine atoms of the absorbing FC(O)OF.

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(12) Launer, P. C. *Instrum. News* **1962**, *13*, 10.

(13) Croce, A. E.; Cobos, C. J.; Castellano, E. *Chem. Phys.* **1996**, *211*, 215.

(14) Zachara, J.; Wisniewski, W. *J. Therm. Anal.* **1995**, *44*, 363.

(15) Porcham, W. U.S. Patent 4,615,872, 1986.

(16) *Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1978.

(17) Heslop, W. R.; Ketelaar, J. A. A.; Büchler, A. *Spectrochim. Acta* **1960**, *16*, 513.