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Regioselectivity in addition of atomic fluorine to alkenes

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Abstract

Irradiation of $N_2F_4(NF_2)$ with propene and with 1,1-difluoroethene in the gas phase at room temperature leads to the addition of F and NF_2 across the double bond. The ratio of terminal to internal addition of F to propene was found to be 1.4:1 after correcting for the decomposition of vibrationally excited intermediates. In the case of 1,1-difluoroethene, the corrected ratio of F addition is 5:1 with addition at the methylene site predominating. The difference in selectivity of F addition to propene and to 1,1-difluoroethene correlates with spin density difference in the π–π^* triplet state of the alkene and with the difference in the HOMO coefficients of the substrate alkene, i.e. the pattern of selectivity is that predicted by the State Correlation Diagram model of Shaik and Canadell.

Introduction

Atomic fluorine, F·, is one of the most reactive intermediates known [1], and should, according to the selectivity–reactivity principle [2], be an indiscriminate species. This is true in gas-phase hydrogen-abstraction reactions [3a, b] from alkanes when atomic fluorine is generated by the photolysis of NF_2 [3a] or from F_2 [3b]. The near-unity hydrogen selectivity ratios shown below for butane illustrate this trend.

Source of F·	Selectivity ratios [3a]			
	CH_3–	CH_2–	CH_2–	CH_3
$F_2 \leftrightarrows 2F$	1	1.3	1.3	1
$NF_2 + h\nu$	1	1.2	1.2	1

To see if this indiscriminate behavior of F· extends to gas-phase addition reactions of unsymmetrically substituted alkenes, we utilized the strategy depicted in Scheme 1 [1]. In this system, F· is generated photochemically from ·NF_2 available from the equilibrium $N_2F_4 \rightleftharpoons 2NF_2$. The F· adducts I

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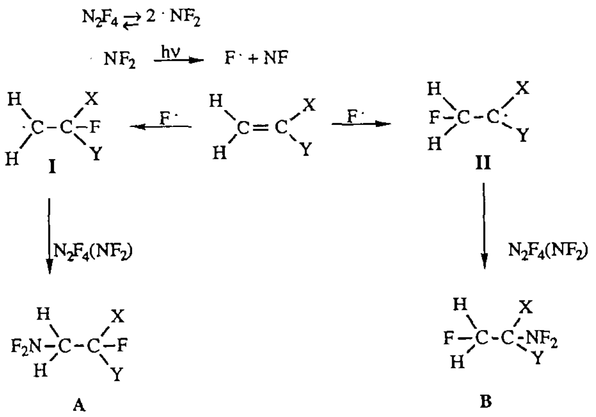
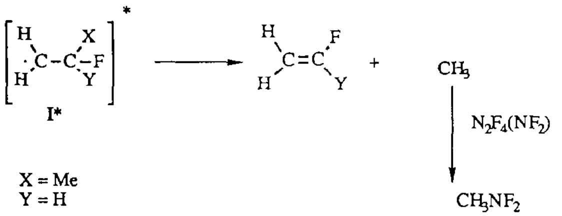


Scheme 1.

and II are converted by the efficient radical trap $N_2F_4(NF_2)$ to a mixture of stable adducts A and B. The molar ratio [A]/[B] is measured and corrected for any unimolecular decomposition of vibrationally excited intermediates as described by Rowland *et al.* [4]. In this paper we report application of this scheme to propene and to 1,1-difluoroethene, and compare the results with those of the Rowland group who studied the same alkenes with F· generated via nuclear recoil [4]. A rationale for the experimental observations is provided by the State Correlation Diagram (SCD) of Shaik and Canadell [5] and by application of the HOMO rule.

Table 1 summarizes our data for propene, where X = Me, Y = H. The molar ratio [B]/[A] was obtained by GC methods and the products identified by ^1H and ^{19}F NMR spectroscopy [3a]. The ratio [II]/[I] was calculated from the relation [B]/([A] + [C]) where [C] is vinyl fluoride concentration resulting from the unimolecular decomposition of the excited intermediate I*.



The fragments, vinyl fluoride and CH_3NF_2, were analyzed by GC methods and identified by ^1H and ^{19}F NMR spectroscopy and via IR spectra [3a]. A comparable cleavage of II to give H· was not observed under these conditions.

According to Table 1, the corrected ratio of terminal to internal addition of F· to propene, i.e. [II]/[I], is 1.4, in excellent agreement with the value of 1.35 found by Rowland *et al.* using ^{18}F· from nuclear recoil [4]. We may conclude therefore that F· addition to propene occurs with little regioselectivity.

TABLE 1

Addition of atomic fluorine to propene; X = Me, Y = H

Initial pressure (Torr)	Molar ratio [B]/[A]	Ratio [II]/[I]
50	1.7	1.4
160	1.6	1.4
580	1.3	1.3

TABLE 2

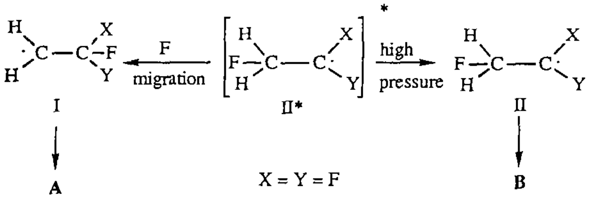
Addition of atomic fluorine to 1,1-difluoroethene, X = Y = F

Initial pressure (Torr)	Molar ratio [B]/[A]
132	0.43
264	0.71
400	1.3

Table 2 presents the results for addition to 1,1-difluoroethene, X = Y = F. The ratios were again determined by GC methods and structures were assigned on the basis of their ^1H and ^{19}F NMR spectra.

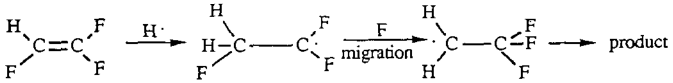
The pressure effect which is obvious from Table 2 suggests that excited intermediates which decompose unimolecularly play an important role in this case in addition; however, we were unable to isolate any fragments. In previous work [6], Rowland *et al.* found that the ratio of $^{18}F\cdot$ attack at the methylene carbon of 1,1-difluoroethene to attack at the fluorinated carbon is *c.* 5 when high pressures of SF_6 are used to quench the excited species. This ratio of 5, therefore, may be taken as the limiting value. Because of safety considerations, we did not make any high pressure runs with the NF_2 system.

One possible explanation for the data in Table 2 is that the $F\cdot$ additions depicted in Scheme 1 become reversible at low pressures. Under these conditions the ratio of [B]/[A] would no longer be under strict kinetic control. However, in the addition of $F\cdot$ to *cis*- and *trans*-2-butene, no isomerization of the starting alkenes was observed [7]. Since reversible $F\cdot$ addition is not important in the 2-butene case, we do not believe reversible addition is significant in the 1,1-difluoroethene reaction. Two other possibilities for the pressure effect apparent from the data listed in Table 2 may be considered. One involves intramolecular fluorine migration within an excited intermediate (Scheme 2).

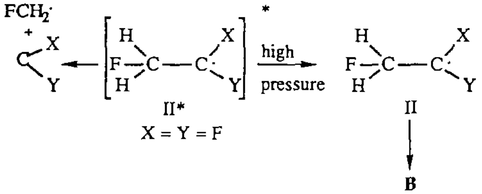


Scheme 2.

This process would require high activation energy, which at elevated pressures would not be available, the excess energy being siphoned off through collisions to yield unactivated II and ultimately B. A recent report [8] of a similar fluorine shift provides a precedent.



Still another explanation for the trend in Table 2 entails C—C cleavage from the excited radical precursor to B (Scheme 3).



Scheme 3.

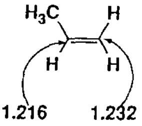
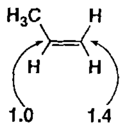
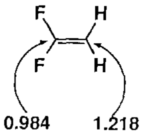
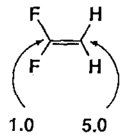
This cleavage process is close to thermoneutral and has been observed in $^{18}F\cdot$ addition [6]. In any event, the 5:1 regioselectivity observed by Rowland *et al.* [6] in the addition of F· to 1,1-difluoroethene at high pressure, where excited intermediates are quenched, is surprisingly large for the 'indiscriminate' fluorine atom.

To find a rationale for the difference in regioselectivity in F· addition to propene and to 1,1-difluoroethene, we examined the State Correlation Diagram (SCD) and the HOMO rule for radical addition to alkenes [5]. Accordingly, Table 3 presents regiochemical correlations with the spin densities of the alkenes, a key feature of the SCD. In Table 4 regiochemical results and the alkene HOMO coefficients are compared. Data in these tables reveal that both the spin densities and HOMO coefficients of the alkenes call for a substantial difference in regioselectivity in going from propene to 1,1-difluoroethene, consistent with the experimental results.

Why do these correlations work in the case of F·? There is a relationship between the spin density in the triplet state of the alkene and the deformation required to get to the transition state (TS) of radical addition. In the case of 1,1-difluoroethene, the lower spin density at the CF_2 end means that substantial deformation is required to attain the TS for addition at this center, even when F· is the attacking radical. The ability of fluorine atoms to remove spin from the carbon to which they are attached may be understood in terms

TABLE 3

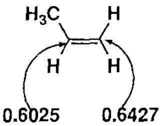
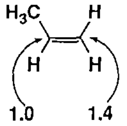
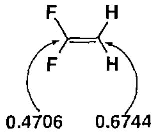
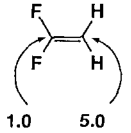
Spin density regiochemistry correlation

Spin densities[a]	Addition of F·[b]
	
	

[a] Ref. 5.
[b] This work and ref. 4.

TABLE 4

HOMO coefficient regiochemistry correlation

HOMO coeff[a]	Addition of F·[b]
	
	

[a] Ref. 5.
[b] This work and ref. 4.

of three-electron stabilization [9]. In contrast, the relatively high spin density at the CH_2 end of 1,1-difluoroethene indicates that the TS for radical addition at this terminus can be reached with less deformation. In propene, the spin densities at each end are almost balanced so little regioselectivity is shown. Since there is a match between spin densities and HOMO coefficients, our results correlate with the latter quantities as well. As a referee pointed out, operation of a repulsive polar effect when F· adds to the CF_2 end of 1,1-difluoroethene would lead to the same result, a greater selectivity of F· addition to 1,1-difluoroethene than to propene. Steric effects should be minimal because of the small size of F. In conclusion, even F· can show selectivity; and, in the addition to propene and 1,1-difluorothene, the pattern of selectivity is that predicted by the SCD and application of the HOMO rule [5].

Experimental

Caution: N_2F_4 and its derivatives should be handled with care. The reactions and isolation operations were conducted routinely behind shields.

General

The ^1H NMR spectra were obtained on a Varian HA-100 spectrometer. Spectra were obtained in $CDCl_3$ with chemical shifts reported in ppm relative to internal TMS. ^{19}F NMR spectra were obtained on a Varian DA 60 spectrometer in $CDCl_3$ with chemical shifts reported in ppm relative to external $CDCl_3$. Negative chemical shifts indicate that the resonances are upfield from $CDCl_3$.

Reaction of N_2F_4 with propene and 1,1-difluoroethene

The photochemical additions of F and NF_2 to the double bond were carried out in the manner described for the photolysis of $N_2F_4(NF_2)$ in the presence of ethene [3a] and of butene [7]. Product isolation and characterization have been reported previously for propene [3a]. Photoproducts from 1,1-difluoroethene were separated by gas chromatography at 0 °C using a 1/4 in. × 20 ft. column containing 30% by weight of SE-30 on 45–60 mesh Chromosorb W. Isomers were identified by trapping out the separated compounds as they emerged from the chromatograph and characterizing them by NMR spectroscopy.

1-Difluoroamino-2,2,2-trifluoroethane (A, X = Y = F): ^1H NMR δ: 4.11 (t, q, $J_{HCF} = 8$ Hz, $J_{HNF} = 26$ Hz) ppm. ^{19}F NMR δ: +58.8 (NF_2); −67.7 (CF_3) ppm.

1-Difluoroamino-1,1,2-trifluoroethane (B, X = Y = F); ^1H NMR δ: 4.18 (d, t, t, $J_{HF} = 56$ Hz, $J_{HCF} = 11$ Hz, $J_{HNF} = 2$ Hz) ppm. ^{19}F NMR δ: 15.6 (NF_2); −113 (CF_2); −242 (CH_2F) ppm. IR, mass spectra and elemental analyses were also consistent with assigned structures.

Tables 1 and 2 summarize the dependence of product ratios on pressure.

Acknowledgment

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