Nangia and Benson[7b] is encouraging as can be more clearly seen from the corresponding values of the ozonolysis of *trans*-2-butene: –51/–54 (ab initio/ref 7b), –2/–3, –54/–53 kcal/mol. (2) The thermochemical character of the PO decomposition changes from being endothermic (ethylene, 1-alkenes) to weakly exothermic (small alkenes) to exothermic (bulky alkenes). According to the Hammond postulate[22] a late, intermediate and early TS II has to be expected. (3) The stereochemistry of the ozonolysis is either *CO controlled* or *PO controlled*. In the former case the larger stability of syn CO and in the latter the magnitude of alkyl–alkyl

interactions in the PO most strongly influence the nature of TS II. In a CO controlled reaction *trans*-alkene FO should be formed irrespective of the alkene configuration. This situation applies to the ozonolysis of small alkenes like 2-butene. In a PO controlled reaction either *cis*- or *trans*-alkene FO are formed, depending on the configuration of the alkene involved in the reaction.

Theoretical Determination of Molecular Structure and Conformation. 9. Ozonolysis of Fluoroalkenes

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Abstract: The Criegee path of the ozonolysis of vinyl fluoride (**1**) and the two 1,2-difluoroethylene isomers (**2, 3**) has been explored with restricted Hartree–Fock and Rayleigh–Schrödinger–Møller–Plesset perturbation calculations. Theoretical results indicate that primary ozonide (PO) formation (step I) and PO decomposition (step II) as well as final ozonide (FO) formation (step III) are all exothermic reactions. For the cis isomer **2**, the computed reaction energies are –57 (I), –8 (II), and –51 kcal/mol (III). The exothermicity of step II results from the relatively strong stabilization of formaldehyde by fluorine. PO, FO, and carbonyl oxide (CO) are also stabilized by F but to a lower extent than $H_2C=O$. F is found to adopt the axial site in puckered conformers of PO and FO due to anomeric stabilization. PO forms with axial F are expected to cleave more easily than those with equatorial F. As a consequence syn fluoro CO should be formed by preference. CO and aldehyde recombine by keeping CF bonds in trans positions. In this way dipole–dipole attraction is maximized. This explains the unusually low cis–trans normal and cross FO ratios obtained upon ozonolyses of **1–3**.

The liquid-phase ozonolysis of haloalkenes has been found to yield a variety of products.[1] Among these are acyl halogenides, acids, diacyl peroxides, anhydrides, haloalkenes, halocyclopropanes, and epoxides. Final ozonides (FO's) result only in vanishing amounts from the ozonation of chloro- and bromoalkenes.[2] In these cases, the Criegee cleavage[3] of the alkene double bond competes with partial cleavage and other side reactions.

Sizable quantities of FO, however, have been obtained upon ozonolysis of vinyl fluoride (**1**) and the two 1,2-difluoroethylenes (cis, **2**; trans, **3**).[4–6] Kuczkowski et al. have estimated Criegee cleavage of **1** to account for 40–85% of the alkene consumption.[6a] Experimental results indicate that the ozonolysis of fluoro- and difluoroalkenes is more similar to the ozonolysis of alkenes than has been found for most other haloalkenes.[4–6] This is also supported by the stereochemistry transmitted from 1,2-difluoroalkenes **2** and **3** to the corresponding FO's. Gilles obtained a cis–trans ozonide ratio of about 10:90 from both *cis*- and *trans*-1,2-difluoroethylene.[4] This is analogous to results observed for *cis*- and *trans*-2-butene, although the stereoselective formation of the trans FO isomer is less pronounced in these cases.[7] Normally, low cis–trans ozonide ratios are observed only for *trans*-alkenes with bulky alkyl substituents. The exceptionally low value obtained

for both **2** and **3** does not fit into this trend. Preponderance of the trans difluoro FO has also been reported for the cross ozonide resulting from vinyl fluoride.[6] This contrasts with the observation that *cis*-2-butene FO is formed upon ozonolysis of propylene.[8]

Gilles[4] and Kuczkowski et al.[6] have analyzed these results on the basis of the orbital symmetry approach.[8] According to these authors the preference for trans configuration for the difluoro normal and cross ozonide can be rationalized in the following way: (1) Fluorine prefers an axial site in the primary ozonide (PO) formed upon ozonation of fluoro- or difluoroalkene. This is due to an anomeric effect involving the C–F bond and the lone pair electrons at the adjacent O atom. (2) The transition state (TS) leading to syn carbonyl oxide (CO) is more favorable than the one leading to anti CO. (3) Dipole–dipole interactions are minimized in the recombination of CO and aldehyde when the C–F bonds are trans to each other. Thus the formation of trans difluoro FO can be explained.[4,6]

In this paper we will examine the stereochemistry of the ozonolyses of fluoroalkenes **1–3** along the lines developed in papers 7 and 8.[9] First we compute restricted Hartree–Fock (RHF) and Rayleigh–Schrödinger–Møller–Plesset (RSMP) ground-state (GS) energies of the molecules involved. Then the effect of the fluorine atoms is discussed on the basis of calculated total energies, molecular orbitals, and electron densities. From the bond separation energies of the formal reaction

$$RF + CH_4 \rightarrow RH + CH_3F$$
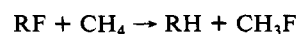
and the thermochemical data for the ozonolysis of ethylene,[9b] energies of reactions I–IV (see paper 8[9b]) are determined for compounds **1–3**. The nature of the TS's for PO decomposition

(1) For a review of the literature on the ozonolysis of halogenated alkenes up to 1976, see: (a) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. I. See also: (b) Sanhueza, E.; Hisatsune, I. C.; Heicklen, J.; *Chem. Rev.* **1976**, *76*, 801–826.

(2) Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 2877–2881.

(3) See, e.g., Criegee, R. *Angew. Chem.* **1975**, *87*, 765–771.

(4) Gillies, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 1276–1287; **1977**, *99*, 7239–7245.

(5) Lattimer, R. P.; Mazur, U.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 4012.

(6) Mazur, U.; Lattimer, R. P.; Lopata, A.; Kuczkowski, R. L. *J. Org. Chem.* **1979**, *44*, 3181–3185. (b) Mazur, U.; Kuczkowski, R. L. *Ibid.* **1979**, *44*, 3185–3188.

(7) See Table VII of ref 1a.

(8) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *J. Am. Chem. Soc.* **1974**, *96*, 348–358.

(9) (a) Cremer, D. *J. Am. Chem. Soc.*, Parts 7 and 8, this issue.

Table I. Absolute Energies and Second-Order Correlation Energies $E^{(2)}$ (hartree) of Compounds Involved in the Ozonolysis of Fluoroalkenes[a]

molecule	config	sym	RHF/B	RHF/C	RSMP/B	RSMP/C	$E^{(2)}$/B	$E^{(2)}$/C
FHC=CH$_2$ (1)		C_s	-176.64601^b	-176.88195^c	-176.95073	-177.31510^c	-0.30472	-0.43450
FHC=CHF (2)	cis	C_{2v}	-275.36143^d	-275.71933^e	-275.78610^d	-276.32402^e	-0.42467^d	-0.60469
FHC=CHF (3)	trans	C_{2h}	-275.36309^d	-275.71960^e	-275.78722^d	-276.32264^e	-0.42413^d	-0.60303
fluoro PO (4)		C_1	-400.72206	-401.28090				
4,5-difluoro PO (5)	cis	C_s	-499.44607	-500.13257				
4,5-difluoro PO (6)	trans	C_1	-499.44523	-500.13181				
FHCOO (7)	syn	C_s	-286.98232	-287.38652	-287.46987	-288.07080	-0.48755	-0.68428
FHCOO (8)	anti	C_s	-286.98307	-287.38764	-287.46741	-288.06830	-0.48434	-0.68066
⌐‾‾‾¬ OCH(F)O (9)		C_s	-287.04759	-287.46221	-287.53550	-288.14539	-0.48791	-0.68318
FHC=O (10)^c		C_s	-212.44566	-212.74784	-212.79757	-213.22926	-0.35723	-0.48494
FHC(=O)OH (11)		C_s	-287.20260	-287.61436	-287.67318		-0.47058	
fluoro FO (12)		C_1	-400.80912	-401.38272				
3,5-difluoro FO (13)	cis	C_1	-499.53888	-500.24162				
3,5-difluoro FO (14)	trans	C_2	-499.54715	-500.24744				
FCH$_3$ (15)^{c,f}		C_{3v}	-138.85861	-139.03461	-139.07752	-139.34266	-0.21993	-0.30883

[a] Except where noted standard molecular geometries are taken.   [b] Energy taken from ref 10.   [c] Optimized geometry.   [d] Reference 15.
[e] Experimental geometry from ref 12.   [f] Energies at standard geometry are -138.85648 (RHF/B; see footnote b), -139.03445 (RHF/C; Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* 1973, *28*, 213–222), -139.07270 (RSMP/B), -139.34204 hartree (RSMP/C).

Table II. RHF and RSMP Bond Separation Energies (kcal/mol) of the Formal Reaction RF + CH$_4$ → RH + CH$_3$F[a]

			RHF		RSMP	
RF	RH	config	B	C	B	C
FHC=CH$_2$	H$_2$C=CH$_2$[b]		5.4	6.8	8.3	9.5
FHC=CHF	FHC=CH$_2$	cis	-0.9	1.2	2.0	2.1
FHC=CHF	FHC=CH$_2$	trans	0.1	1.3	2.7	1.2
fluoro PO	PO		10.1	11.9		
4,5-difluoro PO	fluoro PO	cis	4.4	7.7		
4,5-difluoro PO	fluoro PO	trans	3.9	7.2		
FHCOO	H$_2$COO	syn	0.9	4.3	6.5	8.1
FHCOO		anti	1.4	5.0	5.0	6.6
⌐‾‾‾¬ OCH(F)O	⌐‾‾‾¬ OCH$_2$O^c		12.0	14.4	19.9	20.4
FHC=O	H$_2$C=O		21.5	26.4	27.4	30.6
FHC(=O)OH	H$_2$C(=O)OH		9.5	13.1	14.8	
fluoro FO	FO		15.3	17.0		
3,5-difluoro FO	fluoro FO	cis	8.0	12.2		
3,5-difluoro FO	fluoro FO	trans	13.2	15.9		

[a] Evaluated from energies of Table I and Tables II and III of paper 8.[9b]   [b] RHF/B energy: see footnote a of Table I; RSMP/B energy at standard geometry: -78.10622 hartree.   [c] Basis B energies at standard geometry: -188.31148 (RHF), -188.67153 hartree (RSMP). Basis C energies from ref 20.

Table III. Theoretical Reaction Energies (kcal/mol) of the Ozonolysis of Fluoroalkenes XCH=(Z)CY

reaction	X = F	X = Y = F	X = Z = F
I	-51	-57	-57
II (a, b)	15, -8	-8	-9
III (a, b)	-70, -47	-51	-55
II + III	-55	-59	-64
I + II + III	-106	-116	-121
IVa	-79	-97	-94
IVb	8	-10	-6
IVc	-67	-85	-81
I-IVa	-185	-214	-215
I-IVb	-98	-127	-128
I-IVc	-172	-202	-203

(step II in Scheme 1 of paper 7[9a]) and FO formation (step III) is described on the basis of the Hammond postulate. In order to make qualitative predictions with regard to the stereochemistry, those PO and FO conformers will be investigated which are closest to the TS's.

Results and Discussion

Theoretical energies of compounds **1–14** calculated in this work are given in Table I. Energies of CH$_3$F (**15**) are also shown. The latter are necessary to evaluate the C–F bond separation energies

Table IV. Calculated Heats of Formation ΔH_f° (0°) in kcal/mol

molecule	config	RHF/C	RSMP/C	other source
FHC=CH$_2$ (1)		-30.4^a	-33.1^a	-30.6^b
FHC=CHF (2)	cis	-69.9^a	-70.8^a	-69.7^c
FHC=CHF (3)	trans	-70.0^a	-69.9^a	-74.1^c
fluoro PO (4)		-50.0		-47^d
4,5-difluoro PO (5)	cis	-92.8		-93^d
4,5-difluoro PO (6)	trans	-92.3		-92^d
FHCOO (7)	syn	-4.4	-8.2	
FHCOO (8)	anti	-5.1	-6.7	
⌐‾‾‾¬ OCH(F)O (9)		-48.5	-54.5	
FHC=O (10)		-91.6	-95.8	-90.0^e
FHC(=O)OH (11)	HOCO, syn	-140.0	-141.7	
fluoro FO (12)		-105.1		
3,5-difluoro FO (13)	cis	-155.4		
3,5-difluoro FO (14)	trans	-159.4		
CH$_3$F (15)				-54.1^f

[a] If BSE's are corrected for zero-point vibrational energies (ZPVE's), values become more positive by 0.9 (1, 2) and 1.2 kcal/mol (3).   [b] Experimental value at 298 K taken from: Kolesov, V. P.; Papina, T. S.; *Zh. Fiz. Khim.* 1970, *44*, 1101–1103. This was vibrationally corrected by using observed fundamental vibrational frequencies from: Elst, R.; Rogge, W.; Oskam, A. *Recl. Trav. Chim. Pays-Bas* 1973, *92*, 427–441. Also from: Smith, G. R.; Guillory, W. A. *J. Chem. Phys.* 1975, *63*, 1311–1312. ZPVE (1) 26.8 kcal/mol.   [c] MINDO/3 values from: Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* 1975, *97*, 1307–1311. ZPVE (2) 22.7; ZPVE (3) 22.4 kcal/mol; vibrational frequencies, ref 13b.   [d] Calculated from ΔH_f° (0°) values of ozone and compounds 1–3 and the relevant data of Table III.   [e] Observed ΔH_f° (298°) from: Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* 1971, *37*.   [f] From ref 10.

(BSE's) of Table II. The BSE's have been combined with the results of paper 8 (Table V, reaction energies at the Schrödinger limit[9b]) in order to determine the ab initio reaction energies $\Delta_R E$ shown in Table III. Table IV contains theoretical heats of formation ΔH_f° (0°). They have also been evaluated from BSE's by using known ΔH_f° (0°) values of CH$_4$, CH$_3$F, and compounds RH.[10] Fluoro and difluoro PO and FO conformers, which are relevant to the discussion of TS's of reactions I–III, have been investigated at the RHF/C level. Relative energies, pseudorotation phase angles ϕ, substituent positions, π effects, and dipole moments of these conformers are summarized in Tables V and VI. We now proceed to discuss the fluoro compounds **1–14** in turn.

(10) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* 1971, *93*, 289–300.

Table V. Position and Influence of the F Substituents in Puckered Conformers of Fluorinated Primary Ozonides[a,b]

ϕ, deg	position of F[c]	α_F, deg[c]	rel energy	π_{total}	π_{subst}	π_F	μ, D
4-Fluoro-1,2,3-trioxolane (4) (X = F, Y = Z = H)
0	t-g-axial	26.8	0	-13.1		4.4	3.70
36	t-g-axial	12.7	2.47	-12.8		1.1	4.08
90	t-g-axial	7.6	3.96	-9.8		-0.2	4.22
144	t-g-axial	25.0	2.73	-12.1		1.8	4.04
180	t-g-inclinal	43.7	3.32	-11.2		6.3	3.58
216	t-g-inclinal	57.8	6.11	-3.4		10.5	3.26
270	t-g-equatorial	61.2	7.90	2.6		12.2	3.14
324	t-g-inclinal	44.8	3.14	-4.7		9.2	3.44
cis-4,5-Difluoro-1,2,3-trioxolane (5)
(X = Y = F, Z = H; Y considered)
0	t-g-axial	26.8	0	-7.7	9.8	5.4	3.74
36	t-g-inclinal	44.8	3.64	1.7	15.5	14.6	3.75
90	t-g-equatorial	61.2	7.37	8.1	17.7	17.9	3.60
144	t-g-inclinal	57.8	6.59	2.9	16.8	15.0	3.59
180	t-g-inclinal	43.7	5.92	-2.2	15.3	9.0	3.56
trans-4,5-Difluoro-1,2,3-trioxolane (6)
(X = Z = F, Y = H; Z considered)
0	b-g-inclinal	136.3	0	-10.7	6.8	2.4	2.34
36	b-g-axial	155.0	0.69	-16.1	-2.2	-3.3	3.10
90	b-g-axial	172.4	1.43	-12.8	-3.2	-3.0	3.45
216	b-g-inclinal	135.2	4.43	-1.0	12.9	2.4	1.78
270	b-g-equatorial	118.8	9.28	6.8	16.4	4.2	1.42

[a] Relative energies and π effects are given in kcal/mol. The π effects are derived from the π stabilization energies of 1,2,3-trioxolane.[16a] [b] Energies of the two HOMO's of the planar trioxolanes are -0.5152 and -0.4476 (4), -0.5537 and -0.4711 (5), and -0.5349 and -0.4718 hartree (6), respeceively. [c] For definitions, see ref 18.

Table VI. Position and Influence of the F Substituents in Puckered Conformers of Fluorinated Final Ozonides[a,b]

ϕ, deg	position of F[c]	α_F, deg[c]	rel energy	π_{total}	π_{subst}	π_F	μ, D
3-Fluoro-1,2,4-trioxolane (12) (X = F, Y = Z = H)
0	t-g-inclinal	56.0	7.48	-5.3		8.9	3.33
72	t-g-axial	26.8	0.54	-15.2		0.8	2.74
90	t-g-axial	16.9	0	-18.8		0	2.35
108	t-g-axial	11.7	0.41	-16.6		-0.6	2.07
180	t-g-axial	14.1	2.25	-13.4		0.8	1.89
252	t-g-inclinal	43.9	2.05	-10.6		5.4	1.89
270	t-g-inclinal	54.1	3.08	-10.1		8.7	2.14
288	t-g-inclinal	58.7	4.53	-6.4		9.6	2.47
cis-3,5-Difluoro-1,2,4-trioxolane (13)
(X = Y = F, Z = H; Y considered)
0	t-g-inclinal	56.0	9.20	2.9	17.1	8.2	3.50
72	t-g-inclinal	58.7	2.29	-6.0	10.0	9.2	3.12
90	t-g-inclinal	54.1	1.04	-10.3	8.5	8.5	2.87
108	t-g-inclinal	43.9	0	-10.7	5.3	5.9	2.67
180	t-g-axial	14.1	0.07	-12.4	1.8	1.0	2.37
trans-3,5-Difluoro-1,2,4-trioxolane (14)
(X = Z = F, Y = H; Z considered)
0	b-g-axial	165.9	6.10	-4.4	9.8	0.9	1.75
72	b-g-axial	168.3	0.26	-15.8	0.2	0.6	1.43
90	b-g-axial	163.1	0	-18.9	-0.1	-0.1	1.35
252	b-g-inclinal	121.3	5.56	-2.2	13.8	8.4	0.53
270	b-g-inclinal	125.9	5.68	-3.1	15.7	7.0	0.24

[a] See comment of Table V. [b] Energies of the two HOMO's of the planar trioxolanes are -0.5010 and -0.4549 (12), -0.5364 and -0.4916 (13), and -0.5338 and -0.4940 hartree (14), respectively. [c] For definitions, see ref 18.

Fluoroalkenes (1–3). The geometry of 1 has been optimized with basis C both at the RHF and at the RSMP level. Full details of these calculations will be presented elsewhere.[11] We just note here that RSMP/C structural parameters of 1 [r(C—F) = 132.8, r(C=C) = 135.7 pm; $\angle$CCF = 122.3, $\angle$CCH$_c$ = 121.6, $\angle$CCH$_t$ = 119.6, $\angle$CCH$_g$ = 125.8°] compare well with experimental data determined by electron diffraction (ED).[12] This is why ED geometries of 2 and 3[12] have been used in order to get a reasonable account of F–F interactions in the two 1,2-difluoroethylenes. The cis isomer 2 is correctly predicted as being more stable than the trans isomer, provided an augmented basis is employed at the RSMP level.[11a] Less sophisticated ab initio calculations fail in this respect as is obvious from Table I. The RSMP/C energy difference $E(3)-E(2)$ of 0.9 kcal/mol is close to the thermodynamic value of 1.1 ± 0.1 kcal/mol.[13] Although several qualitative mechanisms have been proposed for the unusual stability of 2,[14] our RSMP/C results are the first that predict relative energies of 2 and 3 in accord with experiment.[11a,15]

Fluorine stabilizes ethylene considerably more than a methyl group (compare with data of Table VII of paper 8[9b]). This is due to its greater π donor ability as has been demonstrated by Radom et al.[10] A second F atom leads to a moderate increase of stability.

Since simultaneous π donation from both F atoms leads to negative π charges at the C atoms which repel each other, the stabilizing interactions between F and the C=C bond cannot double upon incorporation of a second F into ethylene.

Fluoroozonides (4–6, 12–14). The semirigid pseudorotor models of PO and FO[16] have been used in order to investigate fluoroozonide conformers of interest. A standard value of 136 pm has been imposed on the CF bond length.[17]

RHF/C BSE's indicate that the trioxolane ring is significantly stabilized by a fluorine substituent, about 12 kcal/mol in the case of a PO and even 5 kcal/mol more if the FO is substituted. A second F substituent adds another 7 (PO) and 12 kcal/mol (FO), respectively, to the overall stability. This is true, however, only for F being axially positioned. An equatorial fluorine destabilizes the PO ring by 4 and the FO ring by 3 kcal/mol. Hence two equatorially sited F substituents cause an increase in electronic energy which is of the same magnitude as the basis to planarity found for the parent compounds.[16a]

Conformers with equatorial F will be described inadequately within the semirigid pseudorotor model. A more accurate account of the conformational potential of PO's 4–6 and FO's 12–14 is achieved when reoptimizing puckering amplitude q as well as internal and external ring angles for each value of ϕ considered, a procedure which is too costly to carry through at the present.

In order to proceed within the semirigid model we will constrain ourselves to a qualitative discussion based on the π effect.[16b] Since F can act as a π donor, any π-type overlap with the two HOMO's of the trioxolane ring will lead to destabilization. The HOMO's possess highly antibonding character and can only be stabilized by a withdrawal of electrons. Thus, F substitution of a PO or FO should lead to a destabilizing π effect unless its position inhibits overlap with the π-type ring HOMO's. As can be seen from the data of Tables V and VI, the latter situation applies to conformers with axial F (the substituent orientation angle α_F is either $\leq 30°$ or $\geq 150°$[18]). Then even some weak stabilization is indicated by

(11) (a) Cremer, D. *Chem. Phys. Lett.*, in press. (b) Cremer, D., *J. Mol. Struct.*, to be published.

(12) Carlos, J. L., Jr.; Karl, R. R.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177-187. Subscripts denote cis (c), trans (t), and geminal (g) hydrogen.

(13) (a) Craig, N. C.; Entemann, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 3047-3050. (b) Craig, N. C.; Overend, J. *J. Chem. Phys.* **1969**, *51*, 1127-1142.

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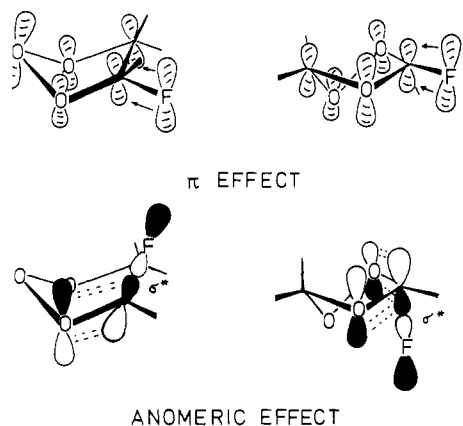(17) Pople, J. A.; Gordon, M. S. *J. Am. Chem. Soc.* **1967**, *89*, 4253-4261.

π EFFECT

ANOMERIC EFFECT

Figure 1. Substituent–ring interactions: π and anomeric effect.

the relative lowering of the two HOMO's.

The π effect of F is responsible for the lower stability of conformers with equatorial substituents. These conformers will reduce their puckering in order to bring F in a more axial position. The antibonding character of the HOMO's, however, will increase with the lowering of q.[16b] Thus the most stable conformer for a given ϕ is puckered to a degree that keeps both π overlap in the ring and ring–substituent π overlap as low as possible. The relative energies computed with the semirigid pseudorotor model represent just upper limits of the true minimal energies at these ϕ values.

Apart from the π-type interactions between substituent and ring, the F atom acts as a σ acceptor, thus reducing negative charges at the oxygen atoms of PO and FO. This leads to the overall stabilization of fluoroozonides as revealed by the BSE's of Table II. Since the electronegativity difference between C and F causes an accumulation of positive (negative) charge on the C (F) atom, charge repulsion will limit the stabilizing effect of a second F substituent. If in addition the CF bond dipoles point in the same direction, dipole–dipole repulsion will also lower the stabilizing effect of the second F. This explains the lower stability of cis FO **13** as compared to its trans isomer **14**.

In the case of PO **6**, the destabilizing effect of one F substituent inclined by 136° with regard to the mean plane of the ring (Table V, PO **6**, $\phi = 0°$) is stronger than dipole–dipole repulsion in the cis form. Therefore **5** is found to be more stable than **6** if conformers at the potential minima are compared. For the fluoro PO's these correspond to the envelope (E) forms at $\phi = 0°$. In these at least one F is axially positioned ($\alpha_F = 27°$, Table V).[19] It is difficult to say at which extent—if at all—F–F steric attraction adds to the stability of **5**. A critical examination of this effect with a more flexible ring model is presently in progress.

Although our calculations overestimate conformational barriers, they provide a reasonable description of stable ozonide conformers. This is confirmed upon comparison of our results with the spectroscopic observations made by Kuczkowski et al.[5] Both theory

and experiment predict **12** to be most stable in its twist form at $\phi = 90°$, i.e., with F occupying the axial site. The same holds for the trans difluoro derivative **14** while the cis isomer **13** adopts a minimal energy somewhere between $\phi = 90$ and $\phi = 180°$ (180° and 270°). Again, this has to do with more axial positions of the F substituents as can be seen from Table VI.

Kuczkowski et al.[5,6] have explained the preference of the axial site in fluoro ozonides by means of the anomeric effect.[20] Previously we have shown in the case of the parent ozonides, namely, ethylene PO and FO, that the same electronic phenomenon is described by π and anomeric effects, utilizing either delocalized or localized MO's.[16b] This is illustrated in Figure 1.

Fluorocarbonyl Oxides and Fluorodioxirane (7–9). The RSMP/C geometry of CO and dioxirane[21] have been used in order to obtain reasonable electronic energies of their fluoro derivatives. CF bond lengths of 133 (**7, 8**) and 136 pm (**9**) have been chosen.[17]

Three observations can be made from the data of Tables I and II: F stabilizes CO to a smaller extent than does a methyl group (Table VII of paper 8[9b]). The opposite is true in the case of dioxirane: Fluorine–ring interactions are twice as large as methyl–ring interactions (RHF/C BSE of methyldioxirane: 8.8 kcal/mol). Thus the energy difference between the dioxirane **9** and the open form **7** is 47 kcal/mol compared to just 34 kcal/mol calculated for the parent compounds.[21] Finally, it is interesting to note that the syn form **7** is more stable than the anti form **8** as has been found also for the methyl CO,[21] but the energy difference between the two isomers **7** and **8** is just 1.5 kcal/mol.

These effects are readily explained when considering the π donor and σ acceptor capacity of F together with the possibility of anomeric stabilization. Although the peroxo group of CO functions as a π acceptor, as is revealed by 2pπ orbital charges in excess of 3e,[22] this property is limited due to Coulomb repulsion between the negatively charged O atoms. The dioxirane **9** gains its stability mainly by donating oxygen lone pair electrons into the C–F bond, thus strengthening the C–O bonds of the dioxirane. Although this effect is partially cancelled by back-donation of electrons from F into the antibonding Walsh orbital of the ring, the net stabilization resulting from anomeric interactions clearly prevails.

The tendency of methyl CO to adopt the syn rather than the anti configuration has been traced to through-space overlap and Coulomb attraction between the terminal oxygen atom and the methyl group.[21] Since F carries a negative charge in **7**, stabilization due to Coulomb attraction is no longer possible in the syn form. Therefore the syn–anti CO energy difference is lowered when the methyl substituent is replaced by F.

Formyl Fluoride and Fluoroformic Acid (10, 11). Interactions between F and O in formyl fluoride have been found to be unusually strong.[10] In order to get reliable results we have completely optimized **10** at all theoretical levels considered (RSMP/C parameters: $r(C—F) = 135.2$, $r(C=O) = 119.3$, $r(C—H) = 109.5$ pm; $\angle FCO = 123.3$, $\angle HCO = 127.5°$; for experimental values see ref 23). The RSMP/C BSE is 30.6 kcal/mol which is somewhat larger than the value derived from heats of formation at 298 ° (24.2 kcal/mol[10]). The RHF/C BSE (26.4 kcal/mol) is in better accordance with experiment.

In fluoroformic acid (**11**) there are two π donors, namely, F and OH, attached to one π acceptor. This limits stabilizing interactions between F and the carbonyl group. The influence of the F substituent is just half as large as found in formyl fluoride.

Thermochemical Data. When comparing the theoretical reaction energies $\Delta_R E$ of Table III with those evaluated for the ozonolysis of ethylene (Table V, paper 8[9b]), it becomes obvious that the exothermicity of the FO formation (I + II + III) increases

(18) The substituent orientation angle α ($0 \leq \alpha \leq 180°$) is defined by cos $\alpha = \vec{s} \cdot \vec{n}$ where $\vec{s}$ is an unit vector pointing from a ring atom to the corresponding substituent S and $\vec{n}$ is the unit vector perpendicular to the mean plane of the ring. For $0 \leq \alpha \leq 30°$, the substituent orientation may be called "t-g-axial", for $150 \leq \alpha \leq 180°$, "b-g-axial", where the prefix t- or b- indicates whether S is on the *top*- or *bottom*side of the ring and the second prefix g (standing for *geometrical*) indicates that the substituent orientation has been calculated with regard to the mean ring plane. For $60 \leq \alpha < 90°$ and $90 < \alpha \leq 120°$, substituent positions are described as "t-" or "b-g-equatorial". Positions with $\vec{s}$ being inclined with regard to the mean plane may be termed "t-" or "b-g-inclinal" ($30 < \alpha < 60°$ or $120 < \alpha < 150°$). See: Cremer, D. *Isreal J. Chem.* **1980**, *20*, 12–19.

(19) We note that the somewhat larger stability of **6** at $\phi = 0°$ as compared to $\phi = 90°$ can be predicted utilizing the conformational energies of **4**. The T form of **4** ($\phi = 90°$) is 4 kcal/mol less stable than its E form at $\phi = 0°$. On the other hand, the E form looses 3.3 kcal/mol when adopting its inverted form at $\phi = 180°$. Thus for **6** the difference between E ($\phi = 0°$) and T form ($\phi = 90°$) should narrow to 0.7 kcal/mol or less depending on the slight stabilization eventually caused by the second axial F substituent in the T form. Considering the fact that a rigid pseudorotor model has been employed the computed difference (1.4 kcal/mol) agrees well with this estimate.

(20) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *25*, 527–548. (b) Eliel, E. L. *Angew. Chem.* **1972**, *17*, 779–791. (c) Romers, C.; Altona, C.; Buys, H. R.; Havinga, E. *Top. Stereochem.* **1969**, *4*, 39.

(21) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199–7205.

(22) RHF/C 2pπ orbital charges of **7** (**8**) are O_T, 1.808 (1.829); O_C, 1.481 (1.478); C, 0.738 (0.712); F, 1.900 (1.909) e (T, terminal; C, central).

(23) Leblanc, O. H.; Laurie, V. W.; Gwinn, W. D. *J. Chem. Phys.* **1960**, *33*, 598–600.
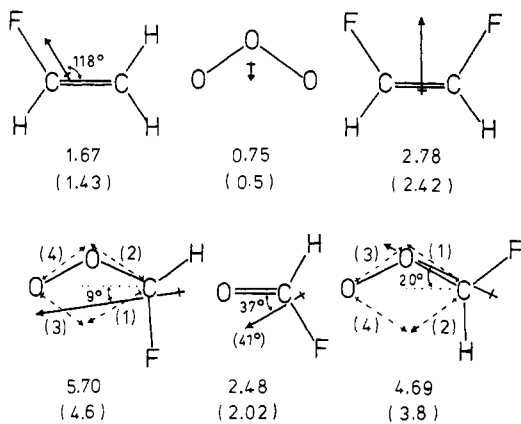
Δ VALUES OF TS II AND TS III

		Δ	ø	CONFIG	ø	Δ
II	(1)	28°	36°	CIS	144°	17°
	(2)	46°	36°	TRANS	216°	57°
III	(3)	226°	108°	CIS	72°	233°
	(4)	152°	72°	TRANS	252°	197°

Figure 2. Calculated dipole moments of fluorinated compounds. Observed values are given in parentheses (for CO values, see ref 26). Dotted arrows indicate the four possible arrangements of the formyl fluoride dipole in TS's II and III. The corresponding Δ values are also given.

by 10–20 kcal/mol upon F substitution. This is also true for the reaction sequence I–IV. Most interesting, however, is the fact that the PO decomposition step II becomes exothermic, provided formyl fluoride is formed. Only if **4** cleaves to **7** and $H_2C\!\!=\!\!O$, is an endothermic reaction to be expected. The relatively high $\Delta_R E(II)$ value of 15 kcal/mol suggests that decomposition of **4** to fluoro CO is not very likely. As a consequence the formation of cross FO from **1** should be moderate. This prediction is in line with experimental observations.[6]

We conclude that in the presence of F substituents PO cleavage proceeds via an early TS. Its properties should be best described by considering PO conformers which are suited for a concerted symmetry-allowed cycloreversion. This will be done in the following section.

Stereochemistry. We analyze the stereochemical features by discussing the three steps of the Criegee mechanism in turn. There are two reasons to expect the endo TS Ia (Figure 1, paper 7[9a]) when adding ozone either to **1** or to **2**. First, dipole–dipole interactions ar attractive in these cases as becomes obvious from the directions of dipole moments shown in Figure 2. Secondly, the endo TS Ia may gain some additional stabilization due to bonding HOMO–LUMO overlap involving F and the central O atom of O_3. This is comparable with the endo effect observed for Diels–Alder reactions.[24]

The endo TS Ia leads directly to the most stable conformers of **4** and **5**, namely, the *E* forms at $\phi = 0°$. Whether this is of any consequence depends on the magnitude of $E_a(II)$ compared to the height of the PO conformational barriers. We have shown that dipole–dipole repulsion between the molecules formed in the decomposition step contributes to the energy of TS II.[9a] The interaction energy can be estimated with the aid of eq 1 of paper 7).[9a,25] The magnitudes of dipole moments of **7**, **8**, and **10** are similar to those of CO and $H_2C\!\!=\!\!O$.[26,27] In a TS with optimal

π overlap their directions may, however, deviate considerably from a parallel alignment as is indicated in Figure 2. Thus decomposition of trans difluoro PO conformers at $\phi = 36$ and 216° leads to a difference $\Delta = \tau_b - \tau_a$ as high as 46 and 57°, respectively, suggesting a significant decrease of $E_a(II)$. We estimate activation energies of step II to range from 8 (decomposition of **6**) to 12 kcal/mol (decomposition of **4** and **5**). Cleavage of **4** to **7** and $H_2C\!\!=\!\!O$ requires a higher $E_a(II)$ due to stronger dipole–dipole repulsion in the TS. $\mu(H_2C\!\!=\!\!O)$ is 0.5 D higher than μ-$(FHC\!\!=\!\!O)$.[27] In addition, dipole orientations of $H_2C\!\!=\!\!O$ and **7** deviate by just 9° (Figure 2).

Within the semirigid rotor model the conformational barriers of PO's **4–6** are all lower than $E_a(II)$ [RHF/C barriers to planarity are 8.75 (**4**), 9.42 (**5**), and 6.46 kcal/mol (**6**)]. Since the computed barriers are certainly upper limits to the true values, it is safe to conclude that conformational processes are much faster than PO cleavage. According to the Curtin–Hammett principle[28] the larger molecular populations in the neighborhood of $\phi = 0°$ do not influence the stereochemistry of step II.

In the case of the difluoro PO's we expect those decomposition paths to be most favorable which start from conformers at $\phi = 36$ and 324 (**5**) or 36 and 144° (**6**). PO forms at these ϕ values are considerably stabilized due to anomeric interactions of an axial F with the ring (vide infra), which should also be of importance in the corresponding TS's. If these PO conformers are decomposed by preference, the CO should be formed in its syn configuration (see Figures 3 and 4 and the corresponding discussion in paper 7[9a]).

Some of the electronic effects which are more important for a late TS may also support the formation of **7**. For example, RHF/C overlap populations indicate that stabilizing F···O interactions typical for the syn configuration of fluoro CO are already developed in the conformers with axial F as has also been found for the 2-butene PO's.[9b]

In the TS of the cycloaddition step dipole–dipole interactions should play a major role. This has also been pointed out by Gillies.[4] We analyze these interactions by looking for the TS which optimizes both π orbital overlap and dipole–dipole attractions. The latter are maximal for a trans arrangement of F substitutents in TS III no matter whether syn or anti fluoro CO is incorporated into the FO. At least this is suggested by the Δ values of 134 (TS IIIa, see Figure 2 of ref 9a), 152 (IIIb), 123 (IIIc), and 162° (IIId).[29] An antiparallel arrangement of molecular dipole moments is best approached in TS's IIIb and IIId both leading to trans FO.

TS IIIb is further stabilized to some extent by favorable anomeric interactions. This conclusion can be drawn when comparing relative energies and π effects of compounds **13** and **14** for $\phi = 72, 108, 252$, or 288° (Table VI, see also Figure 5 of ref 9a). Thus syn CO **7** should almost exclusively be incorporated into trans difluoro FO.

In case of the anti CO **8** π (anomeric) interactions favor TS IIIc (Table VI). Here, however, an early TS is expected, so the π effect should play a minor role. Formation of trans FO **14** should prevail. Putting all the theoretical facts together we predict a relatively high yield of trans FO **14** upon ozonolysis of **2** and **3**. This is in line with experimental observations.[4,6]

Conclusions

In this work we have presented another example on how to describe the TS's of the Criegee path by calculating the properties of the key intermediates of the ozonolysis, namely, PO and CO. Such an approach implies a detailed knowledge of reaction energies $\Delta_R E$ which experimentally are not yet known. Reasonable $\Delta_R E$ values can be determined with the aid of a correlation corrected

(24) For a discussion of the endo rule, see: Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797–869.

(25) For simplicity dipole–dipole interactions are considered to depend on one set of direction angles, namely, τ_a and τ_b. See also eq 1 of paper 7.[9a]

(26) RHF/A dipole moments [3.4 (**7**), 2.7 (**8**), 2.8 D (CO)] are too low and RHF/C dipole moments [5.7 (**7**), 4.7 (**8**), 5.4 D (CO)] are too large due to basis set deficiencies. We estimate the true dipole moments to be close to 4.6 (**7**), 3.8 (**8**), and 4.3 D (CO).

(27) Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", *Natl. Bur. Stand.* **1967**, *10*.

(28) For a discussion of the Curtin–Hammett principle, see: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Interscience: New York, 1965; p 28 and references cited therein.

(29) Note that cos Δ = cos (360 – Δ).

ab initio method. By application of the Hammond postulate it is possible to properly weigh reactant and product properties when describing the TS.

As long as direct calculations of TS's of complex reactions are not feasible at the required level of accuracy, ab initio calculations of reaction intermediates, formed or decomposed in the TS under consideration, can provide an important insight into the reaction mechanisms.

In the case of ozonolysis special consideration has to be given to the conformational processes of the molecules involved. Thus it is not sufficient to calculate just the most stable PO forms. For the fluorinated PO's **4–6** the barriers for conformational changes are predicted to be lower than those for decomposition. According to the Curtin–Hammett principle[28] the higher molecular populations at $\phi = 0°$ are immaterial when looking for the conformers that lead to either syn or anti CO. Instead, those PO forms have to be investigated which are expected to be closest to the TS. In this connection, the assumption of concertedness of reactions I–III is reasonable and helpful.[8] Observing these principles, the stereochemical features of the ozonolyses of **1–3** can be traced to the following electronic effects.

(1) The π donor and σ acceptor ability of F leads to stabilization of PO, CO, aldehyde, and FO. Stabilization is highest for the aldehyde due to the marked π acceptor property of the C=O group.

(2) π donation from an equatorial F destablizes puckered PO's and FO's. This statement is rephrased by saying that fluorine prefers the axial site in ozonides due to favorable anomeric interactions.

(3) Repulsion between the negatively charged F and the terminal O weakens the syn effect observed for CO's.[21]

Because of (1) decomposition of **4–6** is an exothermic step with an early TS. Because of (2) PO's should preferentially cleave via conformers leading to syn CO. Dipole–dipole attraction in TS III favors the formation of trans difluoro FO. Since this applies to both syn and anti CO, the cis–trans FO ratio is unusually low. This was first noted by Gilles.[4] Qualitative arguments put forward on the basis of the orbital symmetry analysis[4,6] are essentially verified by our ab initio results.

Negative Ion States of Terminal Methyl-Substituted Butadienes. Evidence for Through-Space Interactions Involving Methyl Groups

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Abstract: Gas-phase attachment energies, corresponding to the energies of the first and second antibonding π orbitals of terminal methyl-substituted butadienes, were determined by electron-transmission spectroscopy. The data provide evidence for a significant through-space interaction between the hydrogen orbitals of the methyl group and the diene π system and suggest conclusions regarding the conformations of the methyl groups.

The effect of methyl hyperconjugation on the thermodynamic, kinetic, and spectroscopic properties of π electron systems has been of continuing interest for over 4 decades. The purpose of this study is to evaluate the effect of terminal methyl substitution on the energies of the lowest two (π*) negative ion states of 1,3-butadiene. As will be seen, the relatively diffuse character of negative ion states permits the observation of long-range or "through-space" electronic effects which are often not observed in neutral molecules or cations.

The energies of the negative ion states associated with the unfilled π* orbitals of 1,3-butadiene (**1**), *trans*-1,3-pentadiene (**2**),
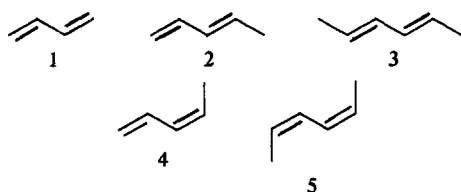
trans,trans-2,4-hexadiene (**3**), *cis*-1,3-pentadiene (**4**), and *cis,-cis*-2,4-hexadiene (**5**) have been measured by electron-transmission

Table I. Electron Affinities and Attachment Energies of Butadiene and Terminal Methyl-Substituted Butadienes

compound	$EA_1{}^a$	$AE_1{}^b$	$AE_2{}^c$
1,3-butadiene (**1**)	−0.65	0.76	2.8
	$−0.62^d$	0.62^d	2.8^d
trans-1,3-pentadiene (**2**)		0.95	2.8
trans,trans-2,4-hexadiene (**3**)		1.13	2.8
cis-1,3-pentadiene (**4**)		0.86	3.1
cis,cis-2,4-hexadiene (**5**)		0.96	3.2

^{a} First electron affinity (±0.05 eV). *^{b}* First attachment energy (±0.05 eV). *^{c}* Second attachment energy (±0.1 eV). *^{d}* Reference 4.

spectroscopy. This technique[2,3] allows for the capture of low-energy (0–10 eV) electrons by a target molecule in the gas phase for periods on the order of 10^{-14} s. The formation of a transient negative ion is observed as a sharp structure or "resonance" in the total electron-scattering cross section as a function of energy.

(1) (a) University of Nebraska–Lincoln; (b) University of Maryland.

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