Theoretical Determination of Molecular Structure and Conformation. 8. Energetics of the Ozonolysis Reaction. Primary Ozonide vs. Carbonyl Oxide Control of Stereochemistry

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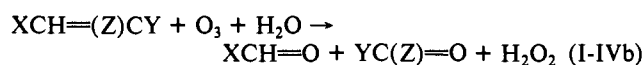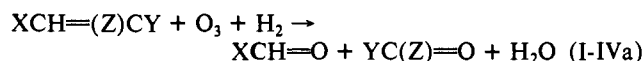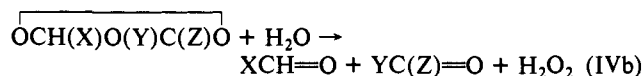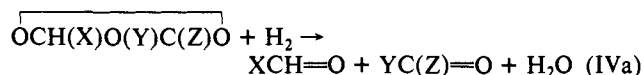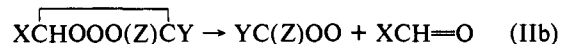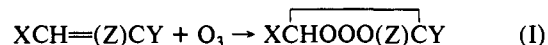
Abstract: Restricted Hartree–Fock (RHF) and Rayleigh–Schrödinger–Møller–Plesset (RSMP) calculations with four different basis sets have been carried out in order to derive a realistic energy profile of the ozonolysis of ethylene. At the highest level of theory employed, reaction energies of −49.2 [formation of primary ozonide (PO), step I], 13.7 [decomposition of PO to formaldehyde and carbonyl oxide (CO), step II], and −63.1 kcal/mol [formation of final ozonide (FO), step III] have been calculated. This corresponds to values of about −49, 11, and −61 kcal/mol at the Schrödinger limit. For the ozonolysis of propylene and 2-butene, reaction energies change by 2–14 kcal/mol, where the largest change applies to step II. Thus, decomposition of *cis*-2-butene PO is slightly exothermic with a reaction energy of −3 kcal/mol. Application of the Hammond postulate indicates that small alkene PO's cleave via a transition state (TS) which favors the formation of syn rather than anti CO ("CO control"). In this case a cis–trans FO ratio lower than unity can be predicted for both *cis*- and *trans*-alkenes. Alkene PO's with bulky substituents decompose via an early TS II resulting from an increased exothermicity of step II. Either syn or anti CO's are formed depending on configuration and conformational behavior of the PO ("PO control"). Syn and anti CO's in turn are stereoselectively incorporated into trans and cis FO's. The change from CO to PO control when increasing the bulk of the alkene explains the anomalous stereochemistry observed for the ozonolysis of small alkenes.

In paper 7 we analyzed the stereochemical features of the ozonolysis reaction.[1] Assuming early transition states (TS's) for the reaction steps I–III of the Criegee mechanism (Scheme I of paper 7[1]), a relationship between the configuration of the alkene and that of the final ozonide (FO) can be derived from ab initio calculations. According to theory, a cis–trans ratio of FO's higher (lower) than unity has to be expected for *cis*- (*trans*-) alkenes with bulky alkyl groups. This is in line with experimental observations.[2] In the case of small alkenes, however, the observed cis–trans FO yields can only be reproduced by theory if a late TS of the primary ozonide (PO) decomposition (step II) is assumed.[1]

In this paper, the location of the TS's in steps I–III is investigated by calculating the energy profile of the ozonolysis of ethylene, propylene, and 2-butene. For this purpose ab initio reaction energies and experimental activation energies are combined. By application of the Hammond postulate it is possible to distinguish between early and late TS's.[1]

Since the thermochemistry of the ozonolysis is not well-known, various attempts have been made to calculate the missing data either from electronic energies[3–5] or from estimated heats of formation.[6,7] The results of these computations are summarized in Table I. Depending on the method the calculated reaction energies vary up to 40 kcal/mol. This is especially true for reaction I and sequence I–III where values based on restricted Hartree–Fock (RHF) theory are significantly more exothermic than those evaluated from empirically derived heats of formation ΔH_f°. As for step II (decomposition of PO), both exothermicity[4] and endothermicity[5,6] have been predicted. The question whether an early or a late TS is traversed in reaction II is difficult to answer on the basis of published data.

We will examine these alternatives by computing the energies of reactions I–IV with four different basis sets both with and

$$XCH{=}(Z)CY + O_3 \rightarrow XCHOOO(Z)CY \qquad (I)$$

$$XCHOOO(Z)CY \rightarrow XCHOO + YC(Z){=}O \qquad (IIa)$$

$$XCHOOO(Z)CY \rightarrow YC(Z)OO + XCH{=}O \qquad (IIb)$$

$$XCHOO + YC(Z){=}O \rightarrow OCH(X)O(Y)C(Z)O \qquad (IIIa)$$

$$YC(Z)OO + XCH{=}O \rightarrow OCH(X)O(Y)C(Z)O \qquad (IIIb)$$

$$OCH(X)O(Y)C(Z)O + H_2 \rightarrow \\ XCH{=}O + YC(Z){=}O + H_2O \quad (IVa)$$

$$OCH(X)O(Y)C(Z)O + H_2O \rightarrow \\ XCH{=}O + YC(Z){=}O + H_2O_2 \quad (IVb)$$

$$OCH(X)O(Y)C(Z)O \rightarrow XC(OH){=}O + YC(Z){=}O \quad (IVc)$$

$$XCH{=}(Z)CY + O_3 + H_2 \rightarrow \\ XCH{=}O + YC(Z){=}O + H_2O \quad (I\text{-}IVa)$$

$$XCH{=}(Z)CY + O_3 + H_2O \rightarrow \\ XCH{=}O + YC(Z){=}O + H_2O_2 \quad (I\text{-}IVb)$$

$$XCH{=}(Z)CY + O_3 \rightarrow XC(OH){=}O + YC(Z){=}O \quad (I\text{-}IVc)$$

without correlation corrections. In this way, it will be possible to extrapolate to HF limit and Schrödinger energies. Comparison of these results with known experimental values of the reaction sequences I–IV provide an idea on how zero-point vibrations and temperature effects influence theoretical energies.

Numerical Techniques

RHF single-determinant[8] and second-order Rayleigh–Schrödinger–Møller–Plesset (RSMP) perturbation calculations[9]

(1) Cremer, D. *J. Am. Chem. Soc.* **1980**, preceding paper in this issue.
(2) For recent reviews, see: (a) Criegee, R. *Angew. Chem.* **1975**, *87*, 765–771. (b) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1.
(3) Leroy, G.; Sana, M. *Tetrahedron* **1976**, *32*, 1379–1382.
(4) Hiberty, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6088–6092.
(5) Klopman, G.; Andreozzi, P. *Bull. Soc. Chim. Belg.* **1977**, *86*, 481–485.
(6) (a) Wadt, W. R.; Goddard, W. A., III *J. Am. Chem. Soc.* **1975**, *97*, 3004–3021. (b) Harding, L. B.; Goddard, W. A., III *Ibid.* **1978**, *100*, 7180–7188.
(7) (a) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 266. (b) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105–3115.

(8) (a) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69–89. (b) Hall, G. G. *Proc. R. Soc. London, Ser. A* **1951**, *A205*, 541–552.

Table I. Comparison of Theoretically Calculated and Empirically Estimated Reaction Energies (kcal/mol)

authors	I	II	III	II + III	I + II + III	method/basis	ref
Leroy, Sana	-93					HF/small basis	3
Hiberty	-97	31				HF/small basis	4
	-41	-8				HF mixed with limited CI[a]	
Klopman, Andreozzi	-87	26	-63	-37	-123	MINDO/3	5
Wadt, Goddard	-52	27	-63	-36	-88 ⎫	empirical estimates	6a
Harding, Goddard	-53	10	-54	-44	-97 ⎭	mixed with GVB[b]	6b
Benson	-45 ± 6	≤14	≥-75	-61	-106 ⎫	thermochemical	7a
Nangia, Benson[d]	-54	-3	-53	-56	-110 ⎭	estimates[c]	7b
Cremer	-49	11	-61	-50	-99 ⎫		this
Cremer[d]	-51	-2	-54	-56	-107 ⎭	Schrödinger limit	work

^{a} Energies of RHF calculations are mixed with those obtained from 3X3 and 6X6 CI computations. ^{b} GVB calculations performed for two and three heavy atom molecules only. ^{c} From group additivities. ^{d} Calculated *trans*-2-butene.

Table II. RHF Energies (hartree) of Molecules Involved in Reactions I–V

molecule	config	conform^a	sym	basis A STO-3G^b	basis B [3s2p/2s]	basis C [3s2p1d/2s]	basis D [4s3p1d/2s1p]	HF limit
ozone			C_{2v}	-221.28961	-223.90982	-224.26143	-224.32929	-224.391
ethylene			D_{2h}	-77.07396	-77.92216	-78.03172	-78.05530	-78.080
propylene		stag	C_s	-115.65804	-116.90331	-117.07001		-117.135
2-butene	trans	stag	C_{2v}	-154.24527	-155.88648	-156.10980		-156.190
2-butene	cis	stag	C_{2h}	-154.24237	-155.88357	-156.10672		
ethylene PO		E	C_s	-298.60620	-301.98900	-302.42252	-302.50832	-302.588
propylene PO		E	C_1	-337.19064	-340.97384	-341.46296		-341.643
2-butene PO	trans	E	C_1	-375.77484	-379.95837	-380.50307		-380.698
2-butene PO	cis	E	C_s	-375.77352	-379.95545	-380.50082		
carbonyl oxide			C_s	-186.04899	-188.26388	-188.54034	-188.59723	-188.649
methyl carbonyl oxide	syn	ecl	C_s	-224.64210	-227.26012	-227.59245		-227.720
methyl carbonyl oxide	anti	stag	C_s	-224.64001	-227.25612	-227.58873		
formaldehyde			C_{2v}	-112.35435	-113.69262	-113.86633	-113.90014	-113.932
acetaldehyde		stag	C_s	-150.94366	-152.68622	-152.91477		-153.006
ethylene FO		T	C_2	-298.63855	-302.06788	-302.51623	-302.59959	-302.680
propylene FO		T	C_1	-337.22647	-341.05735	-341.56057		-341.735
2-butene FO	trans	T	C_2	-375.81429	-380.04650	-380.60510		-380.790
2-butene FO	cis	T	C_1	-375.81333	-380.04596	-380.60387		
hydrogen			$D_{\infty h}$	-1.11751	-1.12683	-1.12683	-1.13133	-1.1336
water			C_{2v}	-74.96590	-75.90864	-76.01075	-76.04935	-76.070
hydrogen peroxide		skew	C_2	-148.76500	-150.55991	-150.76478	-150.82424	-150.860
formic acid		OCOH, cis	C_s	-186.21060	-188.47060	-188.76231	-188.82103	-188.874
methane			T_d	-39.72686	-40.13977	-40.19517	-40.20842	-40.219
ethane		stag	D_{3d}	-78.30618	-79.11593	-79.22875		-79.270

^{a} Designations "staggered" and "eclipsed" refer to the conformation of the group >CHCH$_3$. ^{b} RHF/A energies of one and two heavy atom systems from: Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* 1974, 2, 175–261.

have been carried out for all molecules involved in the ozonolysis of ethylene, propylene, and 2-butene (reactions I–IV). At the RHF and RSMP level, the three basis sets A, B, and C described in paper 7[1] have been employed. In addition, a fourth basis set D was used. This corresponds to Dunning's augmented double-ζ (9s5p1d/4s1p)[4s3p1d/2s1p] basis[10] which we have completely rescaled for ab initio studies on polyoxides.[11]

The geometries of molecules containing less than three heavy atoms have been totally optimized at all theoretical levels considered.[12] This was also done for ozone.[12] In the case of the five-membered ozonides, RHF geometries[13] have been used at the RSMP level too. For the carbonyl oxides (CO's) the RSMP/C geometry of CH$_2$O$_2$ was taken, since RHF and RSMP/small basis calculations lead to unreasonable structures.[14] Finally, the geometry of propene, 2-butene, and acetaldehyde was partially optimized at the RHF/B level. The optimized parameters are $r(C—C) = 150.4$, $r(C=C) = 132.1$ pm, $\angle CCC = 123.6°$

(propene); $r(C—C) = 150.5$, $r(C=C) = 131.8$ pm, $\angle CCC = 125.1°$, $\angle C—CH_{ip} = 111.6$ (*trans*-2-butene, H_{ip}, methyl hydrogen which lies in heavy atom plane); $r(C—C) = 150.6$, $r(C=C) = 131.9$ pm, $\angle CCC = 127.5$, $\angle C—CH_{ip} = 112.6°$ (*cis*-2-butene); $r(C—C) = 149.6$, $r(C=O) = 121.0$ pm, $\angle CCO = 124.2$, $\angle O=CH = 119.7°$ (acetaldehyde). The remaining structural parameters have been kept at standard values.[15]

The HF limit energies have been obtained by extrapolation techniques as described previously.[16] Using correlation energy increments for bonded pairs of atoms derived in ref 16, correlation corrections of the HF limit energies have been evaluated. These lead to approximate Schrödinger energies which may be considered as the RSMP limit energies of perturbation calculations up to nth order performed with m basis functions where n and m approach infinity. Uncertainties of limit energies are expected to stay below 0.01 hartree. Where possible this has been tested using known $\Delta H_f°$ (0°) values and vibrational corrections.

Results and Discussion

RHF, RSMP, and correlation energies of molecules involved in the ozonolysis of ethylene, propylene, and 2-butene are recorded in Tables II–IV. Energies of methane and ethane have been added. Theoretical energies $\Delta_R E$ of reactions I–IV for X = Y = Z = H are summarized in Table V. Table VI provides an

(9) Møller, C.; Plesset, M. S. *Phys. Rev.* 1934, 46, 618–622.

(10) Dunning, T. H., Jr. *J. Chem. Phys.* 1970, 53, 2823–2833; 1971, 55, 3958–3966.

(11) Cremer, D. *J. Chem. Phys.* 1978, 69, 4440–4455.

(12) Cremer, D., to be published.

(13) (a) Cremer, D. *J. Chem. Phys.* 1979, 70, 1898–1910. (b) *Ibid.* 1979, 70, 1911–1927. (c) *Ibid.* 1979, 70, 1928–1938.

(14) Cremer, D. *J. Am. Chem. Soc.* 1979, 101, 7199–7205 and references cited therein. The higher stability of syn CO's was first calculated by Rouse (Rouse, R. A. *J. Am. Chem. Soc.* 1974, 96, 5095–5099) using CNDO/2. I thank Professor R. W. Murray for drawing my attention to Rouse's work.

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

(16) Cremer, D. *J. Comp. Chem.*, to be published.

Table III. RSMP Energies (hartree) of Molecules Involved in Reactions I–V

molecule	config	conform[a]	sym	basis A STO-3G	basis B [3s2p/2s]	basis C [3s2p1d/2s]	basis D [4s3p1d/2s1p]	Schrödinger limit
ozone			C_{2v}	−221.53575	−224.39914	−224.87683	−225.05309	−225.423
ethylene			D_{2h}	−77.19628	−78.10622	−78.29431	−78.37512	−78.583
propylene		stag	C_s	−115.83006	−117.17917	−117.46807		−117.895
2-butene	trans	stag	C_{2v}	−154.46774	−156.25524	−156.64362		−157.207
2-butene	cis	stag	C_{2h}	−154.46539	−156.25265			
ethylene PO		E	C_s	−298.82884	−302.56255	−303.24957		−304.084
propylene PO		E	C_1	−337.46499	−341.64235			−343.396
2-butene PO	trans	E	C_1	−376.10122	−380.72190			−382.709
2-butene PO	cis	E	C_s	−376.10023				
carbonyl oxide			C_s	−186.23438	−188.62719	−189.05283	−189.20723	−189.562
methyl carbonyl oxide	syn	ecl	C_s	−224.87583	−227.71207	−228.23742		−228.892
methyl carbonyl oxide	anti	stag	C_s	−224.87365	−227.70679			
formaldehyde			C_{2v}	−112.47613	−113.91684	−114.17494	−114.27194	−114.504
acetaldehyde		stag	C_s	−151.11049	−152.99800	−153.35793		−153.836
ethylene FO		T	C_2	−298.85452	−302.62461	−303.32834		−304.163
propylene FO		T	C_1	−337.49394	−341.71013			−343.476
2-butene FO	trans	T	C_2	−376.13332	−380.79437			−382.789
2-butene FO	cis	T	C_1	−376.13269				
hydrogen			$D_{\infty h}$	−1.13014	−1.14414	−1.14414	−1.15766	−1.1745
water			C_{2v}	−75.00614	−76.03821	−76.19924	−76.29104	−76.433
hydrogen peroxide		skew	C_2	−148.84584	−150.82313	−151.14392	−151.28031	−151.553
formic acid		OCOH, cis	C_s	−186.36453	−188.81730	−189.25185		−189.769
methane			T_d	−39.78352	−40.24048	−40.33704	−40.39200	−40.512
ethane		stag	D_{3d}	−78.41427	−79.30805	−79.50397		−79.820

[a] See footnote *a* in Table II.

Table IV. Second-Order RSMP and Total Correlation Energies (hartree) of Molecules Involved in Reactions I–V

molecule	config	conform[a]	sym	basis A STO-3G	basis B [3s2p/2s]	basis C [3s2p1d/2s]	basis D [4s3p1d/2s1p]	limit[b]
ozone			C_{2v}	−0.26500	−0.50672	−0.63961	−0.74904	−1.032
ethylene			D_{2h}	−0.12569	−0.18561	−0.26326		−0.503
propylene		stag	C_s	−0.17202	−0.27586	−0.39806		−0.760
2-butene	trans	stag	C_{2v}	−0.22246	−0.36876	−0.53382		−1.018
2-butene	cis	stag	C_{2h}	−0.22301	−0.36907			
ethylene PO		E	C_s	−0.22264	−0.57355	−0.82705		−1.496
propylene PO		E	C_1	−0.27435	−0.66881			−1.754
2-butene PO	trans	E	C_1	−0.32638	−0.76394			−2.012
2-butene PO	cis	E	C_s	−0.32671				
carbonyl oxide			C_s	−0.18539	−0.36331	−0.51249		−0.913
methyl carbonyl oxide	syn	ecl	C_s	−0.23364	−0.45068			−1.171
methyl carbonyl oxide	anti	stag	C_s	−0.23373	−0.45195	−0.64497		
formaldehyde			C_{2v}	−0.12621	−0.22823	−0.31117	−0.37467	−0.572
acetaldehyde		stag	C_s	−0.16684	−0.31179	−0.44317		−0.830
ethylene FO		T	C_2	−0.21597	−0.55673	−0.81210		−1.483
propylene FO		T	C_1	−0.26747	−0.65303			−1.741
2-butene FO	trans	T	C_2	−0.31903	−0.74834			−1.999
2-butene FO	cis	T	C_1	−0.31936				
hydrogen			$D_{\infty h}$	−0.01276	−0.01735	−0.01735	−0.02633	−0.0409
water			C_{2v}	−0.04173	−0.13080	−0.18946	−0.24329	−0.363
hydrogen peroxide		skew	C_2	−0.08559	−0.26997	−0.37459	−0.46213	−0.693
formic acid		OCOH, cis	C_s	−0.15393	−0.34670	−0.49302		−0.895
methane			T_d	−0.05753	−0.10111	−0.14197	−0.18358	−0.293
ethane		stag	D_{3d}	−0.10982	−0.19290	−0.27544		−0.550

[a] See footnote *a* of Table II. [b] Estimates of total correlation energies.

Table V. Theoretical Reaction Energies (kcal/mol) Calculated with Various Basis Sets for the Ozonolysis of Ethylene (X = Y = Z = H)

reaction	RHF A	RHF B	RHF C	RHF D	HF limit	RSMP A	RSMP B	RSMP C	Schrödinger limit
I	−152.3	−98.5	−81.2	−77.6	−73	−60.7	−35.9	−49.2	−49
II	127.3	20.4	9.9	6.9	4	74.2	11.6	13.7	11
III	−147.6	−69.9	−68.7	−64.1	−62	−90.4	−50.6	−63.1	−61
II + III	−20.3	−49.5	−58.8	−57.2	−58	−16.2	−39.0	−49.4	−50
I + II + III	−172.6	−148.0	−140.0	−134.8	−131	−76.9	−74.9	−98.6	−99
IVa	51.1	−62.2	−63.0	−74.5	−76	16.5	−64.7	−48.1	−65
IVb	82.0	19.7	18.5	15.3	16	39.3	3.8	21.2	22
IVc	46.2	−59.8	−70.5	−76.3	−79	8.7	−68.7	−61.8	−69
I-IVa	−121.5	−210.2	−203.0	−209.3	−207	−60.4	−139.6	−146.7	−164
I-IVb	−90.6	−128.3	−121.5	−119.5	−115	−37.6	−71.1	−77.4	−77
I-IVc	−126.4	−207.9	−210.5	−211.1	−210	−68.2	−143.6	−160.4	−167

Table VI. Orbital and Correlation Errors of Theoretical Reaction Energies I-IV[a]

reaction	orbital error/RHF				orbital error/RSMP			correlation error			
	A	B	C	D	A	B	C	A	B	C	limit
I	-79	-25	-8	-5	-12	13	0	-92	-63	-32	-24
II	123	16	6	3	63	1	2	53	9	-4	-7
III	-86	-8	-7	-2	-29	10	-2	-57	-19	-6	-1
II + III	38	8	-1	1	34	11	0	-4	-10	-10	-8
I + II + III	-42	-17	-9	-4	22	24	0	-96	-73	-41	-32
IVa	127	14	13	1	82	0	17	35	2	-15	-11
IVb	66	4	3	0	17	-18	-1	43	16	-3	-6
IVc	125	19	8	3	78	0	7	37	9	-9	-10
I-IVa	85	-3	-4	-2	104	24	17	-61	-71	-56	-43
I-IVb	24	-13	-6	-4	39	6	-1	-53	-57	-44	-38
I-IVc	84	2	0	-1	99	23	7	-58	-64	-50	-43

[a] All energies in kcal/mol.

Table VII. RHF Reaction Energies (kcal/mol) of the Formal Reaction V: $RCH_3 + CH_4 \rightarrow RH + C_2H_6$

RCH_3	RH	config	basis A	basis B	basis C
propylene	ethylene		3.0	3.1	3.0
2-butene	propylene	trans	5.0	4.4	3.9
2-butene	propylene	cis	3.1	2.6	2.0
propylene PO	ethylene PO		3.2	5.4	4.3
2-butene PO	propylene PO	trans	3.1	5.3	4.1
2-butene PO	propylene PO	cis	2.2	3.5	2.7
methyl CO	CO	syn	8.6	12.6	11.6
methyl CO	CO	anti	7.3	10.1	9.3
acetaldehyde	formaldehyde		6.3	10.9	9.3
propylene FO	ethylene FO		5.4	8.4	6.8
2-butene FO	propylene FO	trans	5.3	8.2	6.9
2-butene FO	propylene FO	cis	4.7	7.8	6.1

Table VIII. Influence of a Methyl Group on Reaction Energies I-IV[a]

reaction	methyl group	basis A	basis B	basis C
I	X	-0.2	-2.3	-1.3
	X, Z	1.7	-3.2	-1.5
	X, Y	0.7	-3.2	-2.0
II	X	-5.4	-7.2	-7.3
	X, Z	-8.6	-12.8	-12.5
	X, Y	-9.5	-14.6	-13.9
III	X	3.2	4.2	4.8
	X, Z	4.2	6.9	7.2
	X, Y	4.8	7.3	8.0
II + III	X	-2.2	-3.0	-2.5
	X, Z	-4.4	-5.9	-5.3
	X, Y	-4.7	-7.3	-5.9

[a] All energies in kcal/mol. Negative energies indicate that substituents X, Y, or Z make reactions I-III (see Table V) more exothermic (less endothermic).

analysis of $\Delta_R E$ values by depicting orbital and correlation errors. These are defined by the differences

$$\Delta_R(HF)^{orb} = \Delta_R E(RHF/X) - \Delta_R E(HF \text{ limit})$$

$$\Delta_R(RSMP)^{orb} = \Delta_R E(RSMP/X) - \Delta_R E(\text{Schrödinger})$$

$$\Delta_R^{cor} = \Delta_R E(RHF/X) - \Delta_R E(RSMP/X)$$

where X stands for basis A, B, C, or D. Δ values lower or greater than zero indicate the extent to which the theoretical description of either reactant or product molecules is inconsistent with the real situation. These deviations are caused by basis set deficiencies and the neglect of Coulomb correlation characteristic of a finite basis RHF calculation.

The influence of methyl groups on the stability of the various molecules formed and destroyed in the course of the ozonolysis is analyzed with the aid of the formal reaction V. By means of

$$RCH_3 + CH_4 \rightarrow RH + CH_3CH_3 \qquad (V)$$
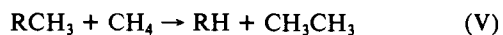
Table IX. Heats of Formation $\Delta H_f^\circ(0^\circ)$ in kcal/mol of Molecules Involved in the Ozonolysis Reaction[a]

compd	X = Y = Z = H	X = CH₃, Y = Z = H	X = Z = CH₃, Y = H	origin
O_3	34.8			expt
XCH=(Z)CY	14.5	8.5	2.1	expt
XCHOO(Z)CY	0	-7	-14	theory
XCH=O	-27.1	-37.1		expt
XCHOO	38	23		theory
OCH(X)O[b]	4	-11		theory
OCH(X)O(Y)C(Z)O	-50	-58	-68	theory

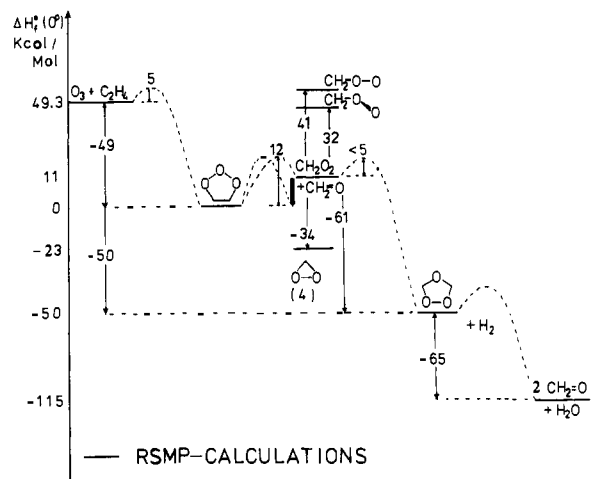[a] Experimental values at 0 K have been evaluated from ΔH_f° (298°) values as described in the text. Theoretical values are based on Schrödinger reaction energies and methyl group effects (Tables II and VIII) using ΔH_f° (0°) of ozone and alkene as reference point. [b] Evaluated from the results of paper 6.[14]

Figure 1. Energy profile of the ozonolysis of ethylene (activation energies have been taken from paper 7[1]).

the C-C bond separation energies of Table VII, changes in $\Delta_R E$ values of reactions I-III can be evaluated for X, Y, and Z being altered to methyl, i.e., the ozonolysis of propylene and 2-butene. These data are shown in Table VIII.

The thermochemical heats of formation of the PO's, CO's, and FO's considered here have been evaluated from Schrödinger reaction energies (Table V) and methyl group effects (Table VIII) by using ozone and alkene ΔH_f° (0°) values as reference points. The latter have been derived from experimental heats of formation at 298 K by correcting for translational, rotational, and vibrational effects. The ΔH_f° (0°) values thus obtained are recorded in Table IX. Heats of formation based on Schrödinger reaction energies are estimated to be uncertain up to 5 kcal/mol, since zero-point vibrations could not be considered in reactions I-III.

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Figure 1 represents a summary of our results by depicting the theoretical energy profile of the ozonolysis of ethylene. Results of paper 6[14] are also considered in Figure 1.

Thermochemical Data for the Ozonolysis of Ethylene. The values of Tables V and VI reveal that neither basis A nor basis B calculations provide reasonable estimates of reaction energies I–IV. Errors caused by basis set deficiencies [$\Delta_R(HF)^{orb}$, Table VI] are significantly larger than 10 kcal/mol. Partial correction for the correlation error of the HF method by second-order RSMP theory leads to a reduction of orbital errors. Obviously, the consideration of all doubly substituted determinants Φ_{ij}^{ab} at the RSMP level has the effect of increasing the flexibility of the basis. This makes it difficult to analyze correlation errors on the basis of RSMP/A and RSMP/B calculations alone. The augmented basis sets C and D lead to more consistent molecular energies. The Δ_R^{orb} values of Table VI clearly show that it is sufficient to apply D at the RHF and C at the RSMP level in order to obtain reasonable reaction energies.[17] Yet, only RSMP/C energies are useful, since correlation errors amount to more than 30 kcal/mol. This is especially true for those reactions which involve ozone. It is well-known that HF calculations on ozone lead to drastic failures, since electron correlation is extremely important for this molecule. Within the MO picture this is indicated by a small HOMO–LUMO energy difference.[14] Because of the large orbital and correlation errors, we constrain our discussion in the following to calculated RSMP/C and estimated Schrödinger energies $\Delta_R E$.

The formation of FO from ozone and ethylene (I + II + III) is a strongly exothermic process. The calculated value of 99 kcal/mol compares well with the 101 kcal/mol found for the ozonolysis of stilbene.[18] The energies of reaction sequences I-IVa, I-Vb, and I-IVc can be derived from experimental ΔH_f° values at 0 K.[19] They are −160.5, −77.4, and −165.1 kcal/mol, respectively. The corresponding theoretical values are evaluated for fixed nuclei. They have to be corrected for zero-point vibrations (I-IVa, +2.9; I-IVb, −0.8; I-IVc, 0.6 kcal/mol), thus leading to values of about −161, −78, and −166 kcal/mol.

Three observations can be made. First, agreement between experimental and estimated Schrödinger $\Delta_R E$ values is satisfying. Second, the RSMP/C reaction energy of sequences I-IVb and I-IVc are close to the Schrödinger value, while it is 17 kcal/mol too positive for sequence I-IVa. We note that basis C does improve description of heavy atoms and heavy atom bonds but not that of H atoms and AH bonds.[20] Therefore, energies of reactions which alter the number of AH bonds come out either too positive or too negative, depending on whether exothermic or endothermic reactions are considered. The former case applies to both reaction IVa and the sequence I-IVa. With a fully augmented basis like D the energy of I-IVa is improved by 10 to −156 kcal/mol. Finally, it has to be pointed out that vibrational corrections appear to be important only for those reactions which involve molecular hydrogen.[21] We conclude that RSMP/C and Schrödinger $\Delta_R E$

Table X. RHF/C Overlap Populations ($\times 10^4$) Computed between the Central Oxygen Atom and the Closest Methyl Hydrogen of Propene and 2-Butene PO[a]

ϕ, deg	propylene PO	2-butene PO	
		cis	trans
0	58	36	57
36	58	66	62
90	12	18	12
144	−2	0	−1
180	−2	−1	−2
216	−2	−2	3
270	−2	−1	−2
324	7	1	6

[a] The methyl group corresponding to substituent X is considered (see Figure 1 of ref 13b). The most positive values are tabulated.

values of reactions I–III are close to vibrationally corrected energies. They provide reasonable estimates of net heats of reaction of the ozonolysis of ethylene carried out in a nonpolar solvent.

Both RSMP/C energies and Schrödinger estimates reveal that the cycloaddition steps I and III are strongly exothermic (−49 and −61 kcal/mol). According to the Hammond postulate,[22] early TS's with reactant properties should be traversed as depicted in Figure 1. This confirms the corresponding assumption made in paper 7.[1] As for the decomposition of ethylene PO, all calculations show that it is endothermic, probably with an $\Delta_R E$ value of about 11 kcal/mol. Similar reaction energies have been suggested by Benson[7a] and Goddard[6] on the basis of ΔH_f° values derived from group additivity tables. We conclude that the TS of step II resembles CO and formaldehyde rather than ethylene PO. The assumption of an early TS II cannot be retained.

Ozonolysis of Propene and 2-Butene. The computed bond separation energies of Table VII range from 2 to 12 kcal/mol. They show that CO and formaldehyde are more stabilized by a methyl group than by FO, PO, or ethylene. The corresponding changes in $\Delta_R E$ values are moderate as far as the exothermic reaction steps are concerned (Table VIII). If propene or 2-butene rather than ethylene are ozonolyzed, step I becomes slightly more exothermic, while the reaction energy of III changes from −61 to −54 kcal/mol. 2-Butene FO's are more stable by −55 (trans) and −56 kcal/mol (cis) than the corresponding PO's. These changes, of course, do not affect the course of the ozonolysis.

More interesting is the decrease of reaction energy II. For propylene the endothermic character is lowered to 4 kcal/mol. In the case of 2-butene it even becomes slightly negative. This means that for small alkenes like 2-butene, 2-pentene, or 3-hexene, TS II will be shifted to the middle between PO and its cleavage products. This is illustrated by Figure 1. In assessing which PO conformer preferentially decomposes, both PO and CO properties have to be considered. A concerted cleavage reaction will most porbably start from PO conformers at ϕ = 36, 144, 216, and 324° (see Figures 3 and 4 in ref 1). The relative energies of these forms differ by less than 1 kcal/mol in the case of 2-butene, 2-pentene, and 3-hexene PO. We have traced the origin of these differences to π-orbital interactions (π effect) between the substituent and the ring; these interactions depend on the position of the substituent which in turn changes smoothly with ϕ.[1] To some extent the π effect is also active in TS II and will either facilitate or impede decomposition of the PO.

On the other hand, syn methyl CO is 3 kcal/mol more stable than its anti isomer.[14] This is due to attractive interactions between the terminal oxygen atom and the methyl group revealed by bonding $O \cdots H_{Me}$ overlap populations. It is interesting to note that bonding overlap populations can also be observed between the central oxygen atom and the methyl hydrogens of propylene and 2-butene PO. As can be seen from the RHF/C values of Table X, overlap populations are most positive for ϕ = 36°. If the second methyl group of 2-butene PO is also considered, conformers at

(17) RSMP/B orbital errors are only accidentally smaller than RSMP/C errors. RSMP/B calculations lead to an artificial elongation of O–O bonds ($r(OO) > 155$ pm); the reason for this has been described in ref 11. By using RHF geometries in all ozonide calculations RSMP/B energies come out too positive by 15–20 kcal/mol. Therefore $\Delta_R E(RSMP/B)$ values are either too positive or too negative by this amount depending on whether an ozonide is formed or decomposed in reactions I–IV. This leads to a fortuitous cancellation of basis set errors as depicted in Table VI.

(18) Dallwigk, E. *Helv. Chim. Acta* **1957**, *40*, 1978–1982.

(19) (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, W. M.; Schuman, R. H. *NBS Tech. Note* **1968**, *270-3*. Zero-point vibrational energies have been evaluated from vibrational frequencies: (c) Shimanouchi, T. *Natl. Ref. Data Ser., Natl. Bur. Stand.* **1972**, *6*. (d) Propene: Silvi, B.; Labarbe, P.; Perchard, J. P. *Spectrochim. Acta, Part A* **1973**, *29*, 263–276. (e) *trans*-2-Butene: Levin, I. W.; Pearce, R. A. R.; Harris, W. C. *J. Chem. Phys.* **1973**, *59*, 3048–3061.

(20) A partially augmented basis like C slightly exaggerates AH bond polarities by artificially dismantling H of charge. Part of this charge is "back-donated" to H by virtue of the p(H) functions used in a fully augmented basis like D. This has been shown in ref 11.

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

(22) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338. For a mathematically based discussion of the Hammond postulate, see: Miller, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 1984–1992.

Table XI.   Theoretical Predictions Concerning the
Stereoselectivity of the Ozonolysis Reaction[a]

alkene config	bulk	nature of TS II	config CO	config FO
ethylene		late		
1-alkenes		late	syn	trans (cis)[b]
cis	small	intermediate	syn	trans (trans)
trans	small	intermediate	syn	trans (trans)
cis	large	early	anti	cis (cis)
trans	large	early	syn	trans (trans)

[a] Experimental observations are given in parentheses. Predominant configuration of CO and FO is given.   [b] Configuration of cross final ozonide.

ϕ = 324 (cis) and 144° (trans) represent further examples of attractive O···CH$_3$ interactions. We have shown that all these PO forms cleave to syn CO.[1] Thus, one feature of the electronic structure of CO is already developed in the PO. According to the principle of least motion, which states that those elementary reactions will be favored that involve the least change in atomic position *and* electronic configuration,[23] the decomposition to syn rather than anti CO should be more favored for a TS II located half-way between PO and PO cleavage products. A preferential formation of syn CO in turn increases the *trans*-alkene FO yield.[1]

Since even large alkyl groups like *tert*-butyl are found to stabilize syn CO more than its anti form, the question arises to what extent, if at all, do the electronic properties of PO play a role in determining the stereochemistry of the ozonolysis. They should be important for an early TS II caused by an exothermic decomposition step. Exothermicity of step II is brought about by either stabilizing the CO and carbonyl moiety or destabilizing the PO by altogether more than 11 kcal/mol. Our calculations on alkyl CO's indicate that not much is gained when going from methyl to ethyl, isopropyl, or *tert*-butyl.[12] 2-Pentene and 3-hexene PO's, on the other hand, are less stale than 2-butene PO's by about 4 kcal/mol according to RHF/A calculations (Table II, Paper 7;[1] Table II, this paper). For *cis*-alkene PO's with bulky alkyl groups, destabilization should even be stronger. We expect reaction energy II to be lowered to −10 kcal/mol. In this situation an early TS adopting PO properties is likely. For *cis*-diisopropyl PO it would mean that anti CO is formed by preference. Anti CO, in turn, tends to react with aldehyde to form cis FO.

As a second consequence of an early TS, the ozonolysis of the corresponding *trans*-alkene, which is known to yield more *trans* FO,[2] should proceed preferentially via the PO conformers at ϕ = 36, 144°. These decompose to syn CO as has been discussed in paper 7.[1]

As far as the stereochemistry of the ozonolysis reaction is concerned, the decomposition of the PO is the most critical step. The corresponding TS may be described as being either "PO controlled" (exothermic reaction) or "CO controlled" (endothermic or weakly exothermic reaction). In the first case, the stereoselectivity of the ozonolysis is a result of (a) a preferential formation of PO in its inverted envelope form at ϕ = 180°, which cleaves via the conformers at 144 and 216° (*cis*-alkenes), and (b) reduced substituent–substituent repulsions in those TS's of step II which are next to the conformers at 36 and 144° (*trans*-alkenes). In the second case, the larger stability of syn CO as compared to its anti form is the determining factor for both *cis*- and *trans*-alkenes. In this way, the anomalous stereochemistry observed for the ozonolysis of small alkenes like 2-butene is resolved. Our stereochemical predictions based on the distinction between early and late TS's II are summarized in Table XI.

Comparison with Experimental Results. Before comparing our predictions with experimental observations a caveat may be appropriate. Strictly speaking our ab initio results apply only to a gas-phase ozonolysis at 0 K. In the gas phase PO is formed as a "hot" molecule with an excess energy of about 54 kcal/mol. Immediate cleavage to a variety of products, as has been discussed,

e.g., by O'Neal and Blumstein[24] or Goddard et al.,[6] is likely. As shown in Figure 1 even formation of the perpendicular $^3A''(3\pi)$ state of CO is feasible. From there, CO can react to dioxirane, its more stable cyclic isomer. That explains why dioxirane rather than PO has been detected when looking for unstable intermediates of the ozonolysis reaction by microwave technique.[25]

In solution-phase ozonolysis the multiplicity of reaction paths is reduced due to heat dissipation at the PO stage. This has convincingly been demonstrated by Nangia and Benson.[7b] The dominance of the Criegee path and the observed stereoselectivity can be considered to be the result of the increased life time of the PO. Nevertheless, non-Criegee reactions or reactions which are not concerted may play a certain though limited role. Consideration of reaction models involving biradical intermediates is probably necessary in order to get a more complete picture of the ozonolysis.[6]

When discussing our ab initio results with regard to solution-phase experiments, we have to ask to what extent (a) temperature effects, (b) entropy differences, (c) solvation energies, and (d) participation of the solvent in the reaction change the calculated energy profile. For the normal ozonolysis carried out at low temperatures in a nonpolar solvent like pentane, significant changes are not expected.[26] On the other hand, it is obvious that due to the complex interplay of reaction conditions and cis–trans FO yields, only a qualitative comparison between theory and experiment is possible. Keeping this in mind our ab initio results can be considered to provide a scheme which affords a rationale for the stereoselectivity of the ozonolysis reaction pertaining to both small and bulky alkenes (Table XI).

This scheme fails, however, to predict cis–trans cross FO ratios observed for 1-alkenes (Table XI). Although no explanation for this failure can be given at present, we feel that it does not invalidate our analysis: Cross ozonides from 1-alkenes are formed in very small yields.[27] Only if a foreign aldehyde present, is the cross ozonide formation increased. Under these conditions predominance of a nonconcerted path with a different stereochemistry can be possible. It would be interesting to investigate how temperature and warmup conditions change the stereochemistry in the case of 1-alkenes like propylene.[28,29]

Finally, it has to be noted that nucleophilic solvents like ether decrease cis–trans ratios for both *cis*- and *trans*-alkenes.[2b] According to Bailey[30] this effect is due to complexation of the CO by the solvent. A nucleophilic attack on the carbon atom of CO may cause a reduction of π delocalization and a lowering of the barrier to rotation. Our finding that CO's are more stable in their syn form seems to support this suggestion.

Conclusions

The major conclusions drawn from this work are as follows: (1) The reaction energies of the ozonolysis of ethylene are −49 (step I), 11 (II), and −61 kcal/mol (III). Agreement with empirical estimates determined from group additivity tables by

(23) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489–496.

(24) O'Neal, H. E.; Blumstein, C. *Int. J. Chem. Kinet.* **1973**, *5*, 397–413.

(25) (a) Lovas, F. J.; Suenram, R. D. *Chem. Phys. Lett.* **1977**, *51*, 453–456. (b) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117–5122.

(26) Solvation energies can be estimated with the aid of the computed dipole moments (ref 1, Tables IV and VII) and structural parameters by using Kirkwood's formula (*J. Chem. Phys.* **1934**, *2*, 351), $\Delta E = -0.2 \, \mu^2/a^3$, where *a* is the cavity radius and the factor 0.2 applies to hydrocarbon solvents with a dielectric constant ϵ of about 2. Although ΔE is very sensitive to the choice of *a* [one half of (largest) molecular diameter plus van der Waals radii of appropriate atoms], it is safe to say that solvation energies are all smaller than 0.5 kcal/mol.

(27) Murray, R. W.; Williams, G. J. *J. Org. Chem.* **1969**, *34*, 1891–1898.

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

(29) Warmup effects have been analyzed by P. S. Bailey et al.[30] in terms of kinetically and thermodynamically controlled reaction steps. Thus, the dependence of the cis–trans ratios on the warmup conditions found for 1,2-diisopropyl- and 1,2-di-*tert*-butylethylene has been explained in ref 30. Since we have not carried out any calculations on the corresponding ozonides, our results provide no basis either to confirm or to disprove Bailey's proposal.

(30) Bailey, P. S.; Ferrell, T. M.; Rustaiyan, A.; Seyhan, S.; Unruh, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 894–898. (b) Bailey, P. S.; Ferrell, T. M. *Ibid.* **1978**, *100*, 899–905.

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

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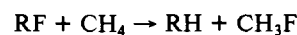
and the thermochemical data for the ozonolysis of ethylene,[9b] energies of reactions I–IV (see paper 8[9b]) are determined for compounds **1–3**. The nature of the TS's for PO decomposition

(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.