NMR ($CDCl_3$) δ 11.1, 26.8, 36.3, 42.4, 46.5, 57.0, 58.6, 127.5, 128.6, 135.9, 151.1, 171.7. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.36; H, 7.44; N, 10.23.

***N*-(Methoxycarbonyl)-2(*S**)-[1′(*S**)-(methoxycarbonyl)ethyl]-4,4-dimethylpyrrolidine (13e: R = CO_2Me)**: bp 120 °C (0.1 mmHg); IR (neat film) 1740 (s), 1705 (s), 1455 (s), 1395 (s), 1200 (s), 775 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 3 H), 1.03 (d, J = 7.1 Hz, 3 H), 1.07 (s, 3 H), 1.42–1.83 (m, 2 H), 2.90 (d, J = 10.7 Hz, 1 H), 3.17–3.76 (m, 2 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 4.32 (ddd, J = 5.5, 8.0, 9.4 Hz; coalescing to d, J = 5.5 Hz, by irradiation at 1.60); ^{13}C NMR ($CDCl_3$) δ 9.3, 25.5, 26.2, 36.8, 40.6, 51.2, 52.0, 58.1, 60.2, 155.6, 174.3. Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.02; H, 9.04; N, 5.74. Found: C, 59.02; H, 8.93; N, 5.80.

***N*-[(Methylamino)carbonyl]-2(*S**)-[1′(*R**)-chloroethyl]-4,4-dimethylpyrrolidine (15e: R = CONHMe)**: mp 137.0–137.5 °C (benzene–hexane); IR (KBr disk) 3370 (s), 1625 (s), 1540 (s), 1380 (s), 1345 (m), 865 (m), 655 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 3 H), 1.13 (s, 3 H), 1.83 (d, J = 6.8 Hz, 3 H), 1.64 (m, 1 H; coalescing to d, J = 11.7 Hz, by irradiation at 4.18), 1.85 (m, 1 H; coalescing to d, J = 11.7 Hz, by irradiation at 4.18), 2.80 (d, J = 4.6 Hz, 3 H), 3.02 (d, J = 9.3 Hz, 1 H), 3.08 (d, J = 9.3 Hz, 1 H), 4.15 (br s, 1 H), 4.18 (dt, J = 2.9, 7.8 Hz, 1 H), 5.00 (dq, J = 2.9, 6.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.0, 25.4, 27.1, 37.7, 38.5, 59.7, 60.3, 61.8, 157.7. Anal. Calcd for $C_{10}H_{19}N_2OCl$: C, 54.91; H, 8.76; N, 12.81; Cl, 16.21. Found: C, 54.97; H, 9.00; N, 12.74; Cl, 16.02.

***N*-[(Phenylamino)carbonyl]-2(*S**)-[1′(*R**)-chloroethyl]-4,4-dimethylpyrrolidine (15e: R = CONHPh)**: mp 170.5–171.2 °C (THF–hexane); IR (KBr disk) 1635 (s), 1450 (m), 1390 (m), 760 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.17 (s, 3 H), 1.38 (d, J = 6.8 Hz, 3 H), 1.72 (dd, J = 12.5, 7.8 Hz, 1 H), 1.93 (dd, J = 12.5, 9.3 Hz, 1 H), 3.20 (s, 2 H), 4.27 (ddd, J = 9.3, 7.8, 2.7 Hz, 1 H), 5.02 (dq, J = 2.7, 6.8 Hz, 1 H), 6.21 (br s, 1 H). Anal. Calcd for $C_{15}H_{21}N_2OCl$: C, 64.16; H, 7.54; N, 9.98; Cl, 12.63. Found: C, 63.97; H, 7.73; N, 9.84; Cl, 12.52.

3,9,9-Trimethyl-1,3-diazabicyclo[4.4.0]decane-2,4-dione (17a): mp 79.0–80.0 °C (benzene–hexane); IR (KBr disk) 1705 (s), 1650 (s), 1440 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 6 H), 1.50 (m, 4 H), 2.31 (d, J = 12.9 Hz, 1 H), 2.51 (dd, J = 10.3, 16.8 Hz, 1 H), 2.83 (dd, J = 5.3, 16.8 Hz, 1 H), 3.19 (m, 1 H), 3.19 (s, 3 H), 4.02 (dd, J = 2.0, 12.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.1, 27.4, 28.8, 29.2, 30.1, 36.6, 37.6, 49.7, 55.4, 154.4, 167.8; mass spectrum, m/z (relative intensity) 210 (M, 20), 195 (20), 141 (100). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.82; H, 8.64; N, 13.32. Found: C, 63.00; H, 8.73; N, 13.20.

***N*-(Tolylsulfonyl)-2-[(methoxycarbonyl)methyl]-5,5-dimethylpiperidine (18a: R = SO_2Tol)**: mp 64.5–65.5 °C (benzene–hexane); IR (KBr disk) 1735 (s), 1340 (s), 1160 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 0.90 (s, 3 H), 1.05–2.05 (m, 4 H), 2.25 (dd, J = 4.2, 15.0 Hz, 1 H), 2.41 (s, 3 H), 2.60 (dd, J = 10.0, 15.0 Hz, 1 H), 2.60 (d, J = 12.9 Hz, 1 H), 3.36 (d, J = 12.9 Hz, 1 H), 3.62 (s, 3 H), 4.47 (m, 1 H), 7.26 (d, J = 8.3 Hz, 2 H), 7.66 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.14; H, 7.44; N, 4.13; S, 9.44. Found: C, 60.11; H, 7.54; N, 4.12; S, 9.50.

***N*-(Methoxycarbonyl)-2-[(methoxycarbonyl)methyl]-5,5-dimethylpiperidine (18a: R = CO_2Me)**: IR (neat film) 1740 (s), 1700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 0.93 (s, 3 H), 1.20–2.21 (m, 4 H), 2.52 (d, J = 7.1 Hz, 2 H), 2.59 (d, J = 13.7 Hz, 1 H), 3.57 (d, J = 13.7 Hz, 1 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 4.73 (q, J = 7.1 Hz, 1 H); high-resolution mass spectrum for $C_{12}H_{21}NO_4$, calcd 243.14700, found m/z (relative intensity) 243.14928 (M, 5), 184 (30), 170 (100).

***N*-(Tolylsulfonyl)-2,2-dimethyl-5-methoxy-6-(methoxycarbonyl)hexylamine (19a: R = SO_2Tol)**: IR (neat film) 3280 (s), 1740 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6 H), 1.31 (m, 4 H), 2.42 (s, 3 H), 2.45 (m, 2 H), 2.65 (d, J = 6.8 Hz, 2 H), 3.33 (s, 3 H), 3.60 (m, 1 H), 3.68 (s, 3 H), 4.70 (t, J = 6.8 Hz, 1 H), 7.30 (d, J = 8.3 Hz, 2 H), 7.74 (d, J = 8.3 Hz, 2 H); mass spectrum, m/z (relative intensity) 371 (M, 1), 266 (20), 216 (65), 184 (95), 155 (100).

***N*-(Methoxycarbonyl)-2,2-dimethyl-5-methoxy-6-(methoxycarbonyl)hexylamine (19a: R = CO_2Me)**: IR (neat film) 3350 (s), 1740–1700 (br s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 6 H), 1.10–1.67 (m, 4 H), 2.42 (dd, J = 15.0, 5.9 Hz, 1 H), 2.57 (dd, J = 15.0, 6.3 Hz, 1 H), 3.01 (d, J = 6.6 Hz, 2 H), 3.34 (s, 3 H), 3.60 (m, 1 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 4.80 (br s, 1 H); mass spectrum, m/z (relative intensity) 275 (M, 1), 242 (10), 212 (12), 187 (15), 170 (20), 155 (100).

3-Methyl-1,3-diaza-8-oxabicyclo[4.4.0]decane-2,4-dione (17c): mp 75.5–76.5 °C (benzene–hexane); IR (KBr disk) 1710 (s), 1660 (s), 1450 (s) cm^{-1}; ^{1}H NMR (benzene-d_6, 400 MHz) δ 1.49 (dd, J = 16.4, 12.8 Hz, H_{5a}), 1.91 (dd, J = 16.4, 4.4 Hz, H_{5e}), 2.41 (dd, J = 11.2, 10.1 Hz, H_{7a}), 2.56 (dddd, J = 12.8, 10.1, 4.4, 3.4 Hz, H_6), 2.59 (ddd, J = 13.3, 12.2, 3.8 Hz, H_{10a}), 3.02 (td, J = 12.2, 2.8 Hz, H_{9a}), 3.17 (ddd, J = 11.2, 3.4, 1.0 Hz, H_{7e}), 3.28 (s, 3 H), 3.50 (ddt, J = 12.2, 3.8, 1.0 Hz, H_{9e}), 3.86 (ddd, J = 13.3, 2.8, 1.0 Hz, H_{10e}). Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.58; N, 15.21. Found: C, 52.31; H, 6.53; N, 15.15.

3-Methyl-8-benzyl-1,3,8-triazabicyclo[4.4.0]decane-2,4,9-trione (17d): mp 152.0–153.0 °C (benzene–hexane); IR (KBr disk) 1715 (s), 1655 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.43 (dd, J = 9.3, 16.8 Hz, 1 H), 2.76 (dd, J = 5.6, 16.8 Hz, 1 H), 3.18 (s, 3 H), 3.28 (m, 2 H), 3.79 (m, 1 H), 4.17 (d, J = 18.4 Hz, 1 H), 4.51 (d, J = 14.4 Hz, 1 H), 4.57 (d, J = 18.4 Hz, 1 H), 4.76 (d, J = 14.4 Hz, 1 H), 7.10–7.45 (m, 5 H). Anal. Calcd for $C_{15}H_{17}N_3O_3$: C, 62.69; H, 5.98; N, 14.62. Found: C, 62.76; H, 5.95, N, 14.62.

Acknowledgment. We acknowledge partial financial support from the Ministry of Education, Science and Culture, the Japanese Government (Grand-in-Aid for Special Project No. 60119002 and 61125002, Scientific Research B No. 61470094, and Grand-in-Aid for Co-operative Research No. 62303003).

Oxygen Donation by an Intermediate in the Reaction of $^{3}CF_2$ with O_2

M. Rahman, Michael L. McKee,* Philip B. Shevlin,* and Renata Sztyrbicka

Contribution from the Department of Chemistry, Auburn University, Auburn University, Alabama 36849.

Received May 18, 1987. Revised Manuscript Received January 23, 1988

Abstract: Reaction of $^{3}CF_2$, produced by reaction of arc-generated carbon atoms with CF_3, with oxygen in the presence of alkenes oxygenates alkenes to epoxides, which are formed stereospecifically, and carbonyl compounds. The reaction is postulated to involve the intermediacy of difluorodioxirane, which transfers oxygen stereospecifically to the alkene. Ab initio calculations demonstrate that the difluorodioxirane is more stable than the corresponding carbonyl oxide and that closure of the carbonyl oxide to the dioxirane should be rapid. The results of these calculations are compared to those on the parent CH_2O_2 system. Reaction of carbon atoms with oxygen and alkenes in the absence of CF_3 gives nonstereospecific epoxidation presumably through the intermediacy of O atoms.

Ever since carbonyl oxides, **1**, were first proposed by Criegee as intermediates in the ozonolysis reaction,[1] there has been growing interest in these species and in their isomers, the dioxiranes **2** and the dioxymethylenes **3**.[2-5] Compounds **1** and **2** appear to have rather different chemistry with **1** reacting predominately by cycloaddition pathways[2-5] and **2** functioning mainly as an oxygen

---

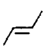
(1) Criegee, R. *Rec. Chem. Prog.* **1957**, *18*, 111.

(2) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(3) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 2, pp 197–276.

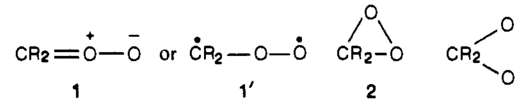
0002-7863/88/1510-4002$01.50/0

Table I. Yields of Epoxides and Carbonyl Compounds in the Reaction of C + O_2 + Alkenes and in the Reaction C + O_2 + CF_4 + Alkenes

reactants, mmol				product yields, mmol × 10^2			
alkene[a]	CF_4	O_2	C	epoxide	aldehyde	ketone	carbonyl/epoxide
=		1.25	5.7	4.0	5.1		1.3
=	25	2.5	5.1	1.2	6.7		5.6
		1.25	4.0	5.0	2.8	1.9	0.9
	25	2.5	5.9	0.2	1.9	1.3	14.6
		1.25	5.8	2.4,[b] 1.2[c]		4.6	1.3
	25	2.5	5.5	5.5,[b] –		15.8	2.9
		1.25	6.2	0.5,[b] 2.5[c]		5.1	1.7
	25	2.5	5.4	–, 4.0[c]		16.0	4.0

[a] In all cases, 15 mmol of alkene were reacted. [b] This is the yield of *cis*-2-butene oxide. [c] The yield of *trans*-2-butene oxide.

atom donor.[6] Although there are some examples of oxygen donation by **1**, its reported chemistry is dominated by investigations of cycloadditions to carbonyl compounds to produce secondary ozonides. While there is little experimental evidence concerning the chemistry of **3**, this species is thought to be involved in the unimolecular decomposition of **2**.[4]



1 **1′** **2** **3**

a, R = H; **b**, R = F

Although the traditional route to **1** is via the ozonolysis of an alkene, this intermediate has also been generated by the reaction of singlet oxygen with diazo compounds[7] and by the reaction of ground-state oxygen with carbenes.[8] We have recently reported that the reaction of atomic carbon with CF_4 leads to CF and $^3CF_2$ by the sequence of reactions shown in eq 1 and 2.[9] A portion

$$C + CF_4 \rightarrow CF + CF_3 \qquad (1)$$

$$C + CF_3 \rightarrow CF + {}^3CF_2 \qquad (2)$$

of the evidence for the intermediacy of $^3CF_2$ was the observation that addition of oxygen to the system resulted in the formation of carbonyl fluoride, **4**, in a reaction known to be characteristic of $^3CF_2$.[10]

The mechanism of carbonyl fluoride formation in the reaction of triplet CF_2 with oxygen has not been elucidated and could involve direct reaction to generate carbonyl fluoride and an oxygen atom as shown in eq 3. An alternate mechanism would involve

$$^3CF_2 + {}^3O_2 \rightarrow \underset{\mathbf{4}}{CF_2{=}O} + O \qquad (3)$$

the intermediacy of CF_2O_2, which, in a second-order reaction, could generate carbonyl fluoride and an oxygen molecule as shown in eq 4. In the present investigation, we report experimental

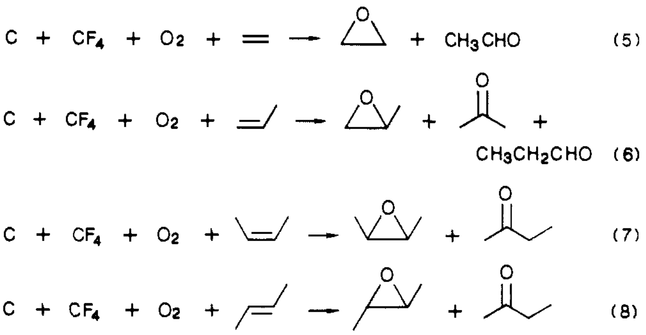
$$^3CF_2 + {}^3O_2 \rightarrow CF_2O_2 \qquad (4)$$

$$2CF_2O_2 \rightarrow 2CF_2{=}O + O_2$$

evidence that indicates that the reaction of $^3CF_2$ with O_2 proceeds with the intermediacy of a CF_2O_2 species, which is capable of donating an oxygen atom to added olefins. In order to evaluate the structure of the CF_2O_2 in this interesting system, we have also carried out ab initio calculations on the energetics of various intermediates and reaction pathways involved.

Results

Reaction of Atomic Carbon with CF_4 and O_2 in the Presence of Olefinic Trapping Agents. The formation of carbonyl fluoride in the reaction of oxygen with $^3CF_2$ by the mechanisms in either eq 3 or eq 4 raises the possibility that either oxygen atoms or CF_2O_2 could be trapped by the addition of appropriate trapping agents. In order to attempt these trapping experiments we have carried out the reaction of arc-generated carbon atoms[11] with CF_4 and oxygen in the presence of alkenes. In these experiments, we have focused our attention on products in which an oxygen has been added to the alkene and have ignored the known products resulting from addition of atomic carbon itself,[11] CF,[9] or $^3CF_2$[9] to the alkene. These experiments gave a mixture of oxygenated products consisting of the olefin epoxide along with aldehyde and/or ketone as shown in eq 5–8. Thus the alkenes are being oxygenated under the reaction conditions, and it is of interest to attempt to determine the nature of the oxygenating species. A previous investigation of the reaction of $^3CF_2$, O_2, and ethylene has reported IR evidence for a carbonyl compound among the reaction products.[12]



It is well known that triplet carbon atoms react with oxygen to generate carbon monoxide and (presumably) an oxygen atom as shown in eq 9.[11] Hence, it is possible that the oxygenated products of eq 5–8 result from reaction of O atoms, generated in the C + O_2 reaction, with alkene. In order to test this possibility, we have reacted carbon atoms with oxygen in the presence of the alkene trapping agents but in the absence of any CF_4. This reaction again resulted in the formation of epoxides and carbonyl compounds but with product ratios and stereochemistries that were different than those observed when CF_4 is included as a reactant. The relative yields of products in this reaction and those in the presence of CF_4 are shown in Table I. An inspection of the data

$$C(^3P) + O_2 \rightarrow CO + O \qquad (9)$$

---

[4] Herron, J. T.; Martinez, R. I.; Huie, R. E. *Int. J. Chem. Kinet.* **1982**, *14*, 201.

[5] Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1.

[6] Murray, R. W.; Jeyaraman, J. *J. Org. Chem.* **1985**, *50*, 2847.

[7] Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 3330.

[8] Murray, R. W.; Suzui, A. *J. Am. Chem. Soc.* **1973**, *95*, 3343.

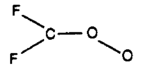
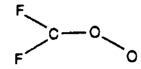
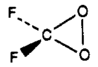
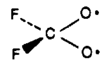
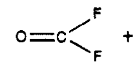
[9] Rahman, M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 6296.

[10] Johnston, T.; Heicklen, J. *J. Chem. Phys.* **1967**, *47*, 475.

[11] For reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. I, pp 1–36.

[12] Saunders, D.; Heicklen, J. *J. Am. Chem. Soc.* **1965**, *87*, 2088.

Table II. Relative Energies (kcal/mol) of Species Optimized at the 3-21G Level on the CF_2O_2 Potential Energy Surface

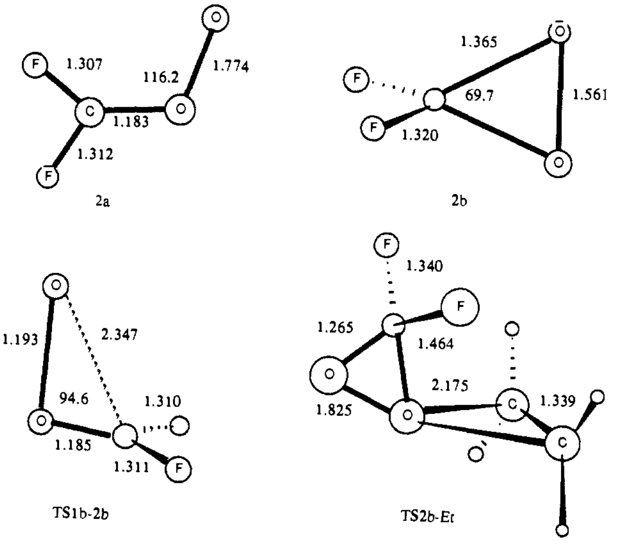
molecule	electronic state	6-31G	MP2/ 6-31G[a]	6-31G*	MP2/ 6-31G*(+ZPC)[a,b]
 **1b**	$^1A'$[c]	9.1	42.7	31.4	68.0 (67.0)
	$^1A'$[d]	35.7	58.1	64.2	80.9 (78.2)
 **1b**	$^3A'$[e]	38.9	81.4	70.1	109.8 (106.8)
 **2b**	$^1A_1$	0.0	0.0	0.0	0.0 (0.0)
 **3b**	$^3B_1$	3.3	6.7	16.5	19.4 (18.1)
	$^3A_2$	47.2	25.0	63.6	40.4 (36.5)
$^1CF_2 + O_2$	$^1A_1$, $^3\Sigma_g^-$	26.1	40.5	41.0	63.2 (58.6)
$^3CF_2 + O_2$	$^3B_1$, $^3\Sigma_g^-$	47.9	79.5	73.2	114.5 (109.8)
 $O{=}CF_2$ + O	$^1A_1$, ^3P	-63.7	-8.8	-40.8	21.7 (19.7)
TS1b-2b	^1A	14.2	52.6	36.0	78.4 (77.4)

[a] For open-shell systems the largest spin contaminant is projected out before evaluating the MP2/6-31G or MP2/6-31G* energies; ref 16. [b] Zero-point corrections are made using vibrational frequencies from the 3-21G level. [c] Closed-shell solution. [d] Open-shell solution with two singly occupied π orbitals. [e] At the 3-21G level the $^3A''$ electronic state is dissociative, decomposing to $F_2C{=}O + O(^3P)$, which is highly exothermic.

in Table I reveals that the ratio of carbonyl compounds to epoxide is invariably higher when CF_4 is included among the reactants and that the epoxides are formed stereospecifically when CF_4 is present. The results of the reactions in the absence of CF_4 may be rationalized by invoking the presence of free oxygen atoms, which are generated by the reaction in eq 9. Although the spin state of the O atoms produced by the process in eq 9 is not known, previous investigations of the reaction of $O(^3P)$ with (*E*)- and (*Z*)-2-butene at 77 K have demonstrated nonstereospecific epoxide formation and have revealed epoxide to carbonyl product ratios similar to those observed here.[13] While the formation of carbon monoxide in the reaction of carbon atoms with oxygen is well documented,[11] these studies mark the first example of trapping of the oxygen atoms generated in this reaction.

An alternative to the involvement of free oxygen atoms in the formation of oxygenated products when carbon, CF_4, and O_2 are condensed with alkenes is an intermediate CF_2O_2, which acts as an oxygen atom donor in this system. When the C + O_2 + ethylene reaction is carried out with perfluoroisobutane in place of CF_4, conditions under which $^3CF_2$ is not generated,[9] oxygenated ethylenes are not observed. This experiment implicates CF_2O_2 as the oxygen donor in this system. Possible structures for CF_2O_2 include the fluoronated carbonyl oxide **1b** or **1b′**, the difluorodioxirane **2b**, or the difluorodioxymethylene **3b**. We have attempted to evaluate the possible intermediacy of species **1b**–**3b** in this system through the use of ab initio calculations.

A Theoretical Investigation of the Reaction between $^3CF_2$ and Oxygen. In these calculations, which utilized the GAUSSIAN 82 program[14a] and the GAUSSIAN 86 program,[14b] geometries were optimized by using the 3-21G basis set at the single configurational level with the restricted Hartree–Fock formulism for closed-shell systems and the unrestricted formulism for open-shell systems.[15] Single-point calculations were made at the MP2/6-31G* level for closed-shell systems and at the PMP2/6-31G* level for open-shell systems where the latter method indicates that the effect of spin contamination has been projected out at the MP2 level.[16] Vibrational frequencies have been calculated at the 3-21G level in order to calculate zero-point energies and to confirm the nature of the stationary points. Geometries of relevant intermediates and transition states are shown in Figure 1. We have also carried out GVB[17] calculations, which can better describe the carbonyl oxides **1a** and **1b** with their strong biradical character. A previous calculation of the structure and vibrational spectrum of **2b** has reported the optimized geometry at the 3-21G level.[18]



2a 2b

TS1b-2b TS2b-Et

Figure 1. 3-21G geometries of relevant intermediates and transition states on the CF_2O_2 energy surface.

The results of these calculations on the CF_2 + O_2 system, shown in Table II, indicate that, at the MP2/6-31G* level, the most

---

[13] Scheer, M. D.; Klein, R. *J. Phys. Chem.* **1969**, *73*, 597.

[14] (a) Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople, J. A. *GAUSSIAN 82*; Carnegie-Mellon University. (b) Frisch, M.; et al. *GAUSSIAN 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Carnegie-Mellon University, Pittsburgh, PA 15213.

[15] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A., *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[16] Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530. Sosa, C.; Schlegel, H. B. *Int. J. Quantum Chem.* **1986**, *29*, 1001.

[17] Bobrowicz; F. W.; Goddard, W. A. In *Method of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4.

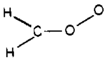
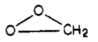
[18] Francisco, J. S.; Williams, I. H. *Chem. Phys.* **1985**, *95*, 71. The geometry and energy of dioxirane **2a** is reported in the following: Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 3rd ed.; Pittsburgh, 1983.

Table III. Relative Energies (kcal/mol) of Species Optimized at the 3-21G Level on the CH_2O_2 Potential Energy Surface[a]

molecule	elec symm	6-31G	MP2/ 6-31G[b]	6-31G*	MP2/ 6-31G*(+ZPC)[b]	GVB(2)/ 6-31G*(+ZPC)	GVB(3/PP)+CI[e]
1a	$^1A'$[c]	5.9	29.4	25.6	51.2 (49.8)	7.6 (6.2)	29.7
1a	$^1A'$[d]	5.5	28.7	22.6	45.0 (40.9)		29.7
2a	$^1A_1$	0.0	0.0	0.0	0.0 (0.0)	0.0	0.0
3a	$^3B_1$	20.3	17.4	31.6	30.2 (29.2)		21.7
3a	$^3A_2$	21.4	9.6	30.0	18.3 (11.9)		13.8
3a	$^3B_2$	−56.3	4.7	−40.8	22.7 (21.2)		12.0
3a	$^1A_1$[f]	−56.3	−0.8	−40.8	12.3 (10.8)		11.1
$^1CH_2 + {}^3O_2$	$^1A_1\ {}^3\Sigma_g^-$	66.7	91.2	72.5	107.3 (98.9)		
$^3CH_2 + {}^3O_2$	$^3B_2\ {}^3\Sigma_g^-$	30.2	61.4	41.6	85.2 (77.1)		
$H_2C{=}O + {}^3O$	$^1A_1\ {}^3P$	−54.0	1.7	−33.3	30.3 (26.7)		
TS1a-2a	^1A	21.2	54.1	41.1	77.0 (74.5)	19.2 (16.7)	

[a] Zero-point corrections are made using vibrational frequencies from the 3-21G level. [b] For open-shell systems the largest spin contaminant is projected out before evaluating the MP2/6-31G or MP2/6-31G* energies; ref 16. [c] Closed-shell solution. [d] Open-shell solution with two singly occupied π orbitals. [e] Partially optimized geometries; ref 22a. [f] Open-shell solution with broken symmetry.

Table IV. A Comparison of the Difference in Energy (kcal/mol) between the Bent and Cyclic Forms of O_3 and CH_2O_2

	3-21G geometry		6-31G* geometry[a]			
	MP2/6-31G*	GVB(2)/6-31G*	GVB(2)(6-31G*)	MP2/6-31G**[a]	MP4SDTQ/6-31G**[a]	other values
O_3 bent	0.0 (19.2)[b,c]		0.0	0.0	0.0	0.0
O_3 cyclic	35.1		61.7	44.0	41.2	28–37[e]
	6.2 (0.0)[b,d]	0.0		0.0	0.0	
	−45.0	−6.2		−41.0	−34.9 (−31.3)[f]	

[a] C. Melius, private communication. [b] Refers to the open-shell solution and the energy evaluated at the PMP2/6-31G* level. This is a lower energy than the closed-shell solution with energy evaluated at the MP2/6-31G* level for H_2CO_2 but a higher energy for O_3. [c] At the 3-21G geometry. [d] At the optimized UHF geometry. [e] Ref 25 and references cited therein. [f] At the MP4SDQ/6-31G*//MP4SDQ/6-31G* level; D. Cremer, private communication.

stable intermediate is **2b**, which is lower in energy than either singlet or triplet **1b** by 67.0 and 106.8 kcal/mol, respectively, and more stable than **3b** by 18.1 kcal/mol. Direct production of O(^3P) by the reaction in eq 3 is calculated to be exothermic by 90.1 kcal/mol as compared to an experimental exothermicity of 80.0 kcal/mol.[19,20]

It is of interest to compare the results of calculations on the CF_2O_2 system with those which have been reported for the CH_2O_2 system. Although there is only one report of theoretical studies of the CF_2O_2 system,[18] numerous theoretical investigations of CH_2O_2 have appeared in the literature.[22] Table III lists our results on this system as well as those obtained by Harding and Goddard[22a] using an ab initio GVB method plus CI. An examination of Table III reveals that our results are qualitatively consistant with the previous theoretical work, which has demonstrated that the parent dioxirane **2a** is more stable than the carbonyl oxide form **1a** by 29.7 kcal/mol.[22a] Our calculation of 40.9 kcal/mol for the energy difference between **1a** and **2a** appears to overestimate this value as compared to the GVB calculation. This is due to the fact that both the zwitterionic and biradical forms of **1a** (**1a** and **1a'**) are known to be important[22] and these are not well represented by the present computational technique. As discussed by Cremer,[22c] a recurring problem in HF calculations of the geometry of **1a** is the fact that this method gives an O–O bond length that seems abnormally long. In order to pursue this point, further GVB calculations were carried out. Use of a larger basis set (GVB(2)/6-31G*) to reoptimize **1a** results in a substantial shortening of the O–O bond to 1.468 Å. However, single-point calculations at the 3-21G and GVB(2)/6-31G* geometries by using the GVB(2)/6-31G* method indicate only a 2.1 kcal/mol lowering of energy. It is clear that the energy is rather insensitive to large distortions in the O–O bond length. An even shorter O–O bond length of 1.295 Å has been reported for **1a** at the MP2/6-31G* level.[22c,23] The fact that the HOMO of **1a** is antibonding along the O–O bond many dictate a longer bond than would be otherwise expected. Despite uncertainties about geometry, all the calculations on the CH_2O_2 system agree in predicting increasing stability as one goes from carbonyl oxide to dioxymethylene to dioxirane.

While it is known that the GVB treatment is preferred for molecules with strong biradical character such as carbonyl oxide and ozone,[24] the method overestimates their stability compared to closed-shell structures. This is illustrated in Table IV where bent and cyclic forms of ozone and carbonyl oxide are compared. The calculated energy difference between bent and cyclic ozone is in the range 28–37 kcal/mol.[25,26] The GVB treatment (without CI) overestimates the stability of the bent form of ozone and leads to a 61.7 kcal/mol energy difference. On the other hand, the MP2 treatment leads to an energy difference in better agreement with the more accurate values.

In the case of carbonyl oxide the cyclic form is predicted to be 35 kcal/mol lower than the bent forms on the basis of calculations at the MP4SDTQ/6-31G**//6-31G* level. Relative to this value, the MP2/6-31G*//3-21G method underestimates the stability of the bent form while the GVB(2)/6-31G* method overestimates the stability of the bent form relative to cyclic form (Table IV).

Since carbonyl oxide is best described as a biradical, a single configurational plus perturbative correlation treatment can be

---

(19) Heats of Formation at 0 K are taken from: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1; *JANAF Thermochemical Tables*, 3rd ed.

(20) Heat of formation of $^3CF_2$ is taken as the heat of formation of $^1CF_2$ (−43.6 kcal/mol)[19] plus the observed singlet–triplet separation of 56.6 kcal/mol,[21] which yields a value of 13.0 kcal/mol.

(21) (a) Koda, S. *Chem. Phys. Lett.* **1978**, *55*, 353. (b) Koda, S. *Chem. Phys.* **1982**, *66*, 383.

(22) (a) Harding, L. B.; Goddard, W. A., III *J. Am. Chem. Soc.* **1978**, *100*, 7180. (b) Kahn, S. D.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1871. (c) Cremer, D. *J. Am. Chem. Soc.* **1979**, *101*, 7199. (d) Hull, L. A. *J. Org. Chem.* **1978**, *43*, 2780. (e) Ha, T.-K.; Kuhne, H.; Vaccani, S.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1974**, *24*, 172.

(23) This value increases to 1.329 Å when the geometry is optimized at the MP4SDQ/6-31G* level; D. Cremer, private communication.

(24) Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley: New York, 1982.

(25) Jones, R. O. *J. Chem. Phys.* **1985**, *82*, 325–332 and references cited therein.

(26) Cremer, D. In *The Chemistry of Funtional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p 1.

Table V. A Comparison of Heats of Reaction (kcal/mol) and Activation Energies (kcal/mol) for the Reactions **1a** → **2a** and **1b** → **2b**

	MP2/ 6-31G*// 3-21G	GVB(2)/ 6-31G*// 3-21G	GVB(2)/ 6-31G*//GVB(2)/ 6-31G*[a]
ΔH_{reactn} (**1a–2a**)	−45.0 (−40.9)[b]	−7.6 (−6.2)[b]	−6.8 (−5.4)[b]
E_a (**TS1a-2a**)	32.0 (33.6)[b]	11.6 (10.5)[b]	
ΔH_{reactn} (**1b–2b**)	−68.0 (−67.0)[b]	−19.0 (−18.0)[b]	
E_a (**TS1b-2b**)	10.4 (10.4)[b]	3.3 (3.3)[b]	

[a] For **1a** the CO distance is 1.218 Å and the OO distance is 1.468 Å. For **2a** the CO distances are 1.358 Å and the OO distance is 1.446 Å. [b] The values in parentheses are corrected for differences in zero-point energies, which are calculated with 3-21G frequencies.

Table VI. Relative Energy (kcal/mol) for Species Involved in Oxygen Atom Transfer from **2a** and **2b** to Ethylene

	6-31G	MP2/ 6-31G	6-31G*	MP2/ 6-31G*(+ZPC)[a]
2a + =	0.0	0.0	0.0	0.0 (0.0)
TS2a-Et	18.2	34.6	36.2	51.7 (51.1)
 + $H_2C{=}O$	−53.8	−47.5	−62.4	−55.4 (−55.0)
2b + =	0.0	0.0	0.0	0.0 (0.0)
TS2b-Et	9.2	−2.4	23.3	6.6 (7.2)
 + $F_2C{=}O$	−63.5	−58.1	−69.8	−64.0 (−62.6)

[a] Zero-point corrections are made with vibrational frequencies from the 3-21G level.

improved by choosing the dominant configuration as the reference solution for adding correlation. In the ground state of carbonyl oxide ($^1A_1$), this is the open-shell solution with two singly occupied π orbitals. The spin projected PMP2/6-31G* energy of the UHF solution (which is highly spin contaminated) is lower than the MP2/6-31G* energy, which is based on the RHF solution. In contrast, the RHF solution provides a better starting point for perturbative correlation than the UHF solution for F_2COO (Table II; **1b**), indicating a smaller degree of biradical character. In our discussions of energetics, we will use the PMP2/6-31G* value for **1a** and the MP2/6-31G* value for **1b**.

In Table V the heats of reaction and the activation energies are given for the reactions **1a** → **2a** and **1b** → **2b**. For the fluorinated system, the carbonyl oxide **1b** is probably calculated to be too unstable with respect to **2b** at the MP2/6-31G* level (ΔH_{reactn} = 67.0 kcal/mol; Table V) due to the fact that the contributions of **1b** and **1b′** are poorly estimated. On the other hand, the GVB(2)/6-31G*//3-21G difference of 18.0 kcal/mol is probably an underestimation. The important point, however, is that both methods find a much larger stabilization for the fluorinated dioxirane than found for the parent CH_2O_2 system.

In a similar fashion, the barriers to closure of both **1a** and **1b** are lower when calculated by the GVB method than when calculated by MP2/6-31G* (Table V). However, both computational methods predict a lower barrier to ring closure for **1b** than **1a**. We have also calculated transition-state energies for the transfer of oxygen to ethylene from both **2a** and **2b**, and these are listed in Table VI.

An interesting aspect of the fluorinated system is the increased stability of singlet **1b** relative to triplet (67.0 − 106.8 = −39.8 kcal/mol, Table II) as compared to the splitting calculated by Harding and Goddard in **1a** of −27.7 kcal/mol.[22a] This is due to the destabilization of the LUMO (which is singly occupied in the triplet) through interaction with the fluorine lone pairs. The effect is even more dramatic for the singlet–triplet splitting in the carbenes CH_2 and CF_2 where fluorine stabilizes singlet methylene by 65.6 kcal/mol (S–T(CH_2) = 9 kcal/mol;[27] S–T(CF_2) = −56.6 kcal/mol).[21]

Discussion

The results of the experimental part of this study indicate that alkenes are oxygenated when condensed with C + CF_4 + O_2 at 77 K, and we must consider the nature of the oxygenating species. Although the calculations indicate that it is thermodynamically feasable for $^3CF_2$ to react with O_2 to generate carbonyl fluoride and an oxygen atom, the experimental results indicate that free oxygen atoms are not involved in the C + CF_4 + O_2 system. The fact that an oxygen atom has been transferred to the alkene to give stereospecific epoxide formation rules out the intermediacy of O(^{3}P) atoms produced by the mechanism in eq 5.[13] In addition, the intermediacy of O(^{1}D) can be ruled out since the chemistry of O(^{1}D) is characterized by C–H insertion to give alcohols.[28] No alcohols are observed in the present reactions despite the fact that insertion into the allylic C–H bonds of the alkenes present should be particularly facile.

Since free oxygen atoms are not the oxygenating species in this system, we must postulate that either CF, CF_2, or CF_3 react with O_2 to generate an intermediate, which will donate an oxygen to the alkenes. Possible candidates for this CF_xO_y intermediate include CFO, CFO_2, CF_2O_2, CF_3O, and CF_3O_2. We have demonstrated that, when C atoms are reacted with perfluoroisobutane, neither CF_2 nor CF_3 is generated and alkene addition products are derived solely from CF.[9] The fact that no oxygenated alkenes are observed when O_2 is added to the C + perfluoroisobutane + ethylene system appears to rule out oxygen donors CFO and CFO_2 (from CF + O_2) as intermediates in the alkene oxygenations.

The possibility of either CF_3O or CF_3O_2 reacting with alkenes to generate epoxides stereospecifically seems unlikely. The reaction of CF_3O with alkenes has been observed and is a simple radical addition reaction.[29] While reaction of CF_3 with O_2 does generate CF_3O_2,[30] there is no evidence that this species will react with alkenes to generate epoxides stereospecifically. We thus conclude that the most likely oxygenating species in this system is CF_2O_2.

Since our results are best accommodated by an intermediate CF_2O_2, which is capable of transferring oxygen to added alkenes, it is instructive to consider the structure of this intermediate. Although dioxiranes have been isolated[6,31] while carbonyl oxides have not, both carbonyl oxides[7,8] and dioxiranes have been observed to react with alkenes to generate epoxides. In fact, the ozonolysis of tetrafluoroethylene, which may be expected to generate an intermediate CF_2O_2, leads to high yields of tetrafluoroethylene oxide.[32] However, epoxidation of alkenes with carbonyl oxides generally leads to stereoselective rather than stereospecific epoxide formation. An examination of the stereochemistry of epoxide formation has been suggested as a method of determining if the reagent transferring the oxygen atom is a carbonyl oxide or a dioxirane.[6] The stereospecific epoxide formation in our system as well as the results of our calculations lead us to conclude that the species responsible for epoxide formation in the reaction of C + CF_4 + O_2 + alkenes is the difluorodioxirane **2b**. Although the energy difference between **1b** and **2b** of 67.0 kcal/mol calculated at the MP2/6-31G* level may be too large for the reasons mentioned above, we feel that the magnitude of this energy gap is great enough to ensure that **2b** is more stable than **1b**.

Thus, it appears that CF_2O_2, whether generated by the reaction of the carbene with oxygen or in the ozonolysis of C_2F_4, exhibits the chemistry expected of the dioxirane. This behavior is in contrast to that of other systems in which distinctly different reactivity is observed for the carbonyl oxide and the dioxirane. In such cases, it must be assumed that conversion of the carbonyl oxide to the dioxirane is slow reactive to its intermolecular reaction

---

(27) Experimental singlet–triplet splitting in CH_2: Bunker, P. R.; Jensen, P.; Kraemer, W. P.; Beardsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724.

(28) Yamazaki, H.; Cvetanovic, R. J. *J. Chem. Phys.* **1964**, 41, 3703.

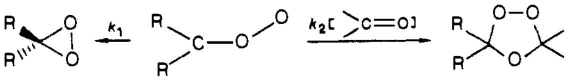
(29) Chen, K. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1383.

(30) (a) Clemitshaw, K. C.; Sodeau, J. R. *J. Phys. Chem.* **1987**, *91*, 3650. (b) Butler, R.; Snelson, A. *J. Phys. Chem.* **1979**, *83*, 3243. (c) Ryan, K. R.; Plumb, I. C. *J. Phys. Chem.* **1982**, *86*, 4678. (d) Carlap, F.; Lesclaux, R.; Dognon, A. M. *Chem. Phys. Lett.* **1986**, *129*, 433.

(31) (a) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117. (b) Lovas, F. J.; Suenram, *Chem. Phys. Lett.* **1977**, *51*, 453. (c) Martinez, R. I.; Huie, R. E.; Herron, J. T. *Chem. Phys. Lett.* **1977**, *51*, 457.

(32) Agopovich, J. W.; Gillies, C. W. *J. Am. Chem. Soc.* **1980**, *102*, 7572.

as a 1,3-dipole. If we assume, as indicated by numerous calculations,[22] that dioxiranes are more stable than carbonyl oxides, a molecule that is generated as an initial carbonyl oxide (by ozonolysis of an alkene for example) will react as such if k_2[>CO] > k_1 in eq 10.



(10)

Competition between ring closure and $4\pi + 2\pi$ cycloaddition in **1a** and alkyl-substituted carbonyl oxides has been considered in some detail, and it is generally agreed that the rate of cycloaddition is far greater than that of ring closure in these systems.[4] In fact, it has been estimated that $k_2/k_1 = 10^{11}$ in acetaldehyde oxide.[4] Reported calculations of the barrier to ring closure in **1a** range from 27.2 kcal/mol by a semiempirical method[22d] to 16.8 kcal/mol obtained from an ab initio calculation.[22e] In the present work, we have calculated a barrier of 33.6 kcal at the MP2/6-31G* level for the closure of **1a**. However, this value drops to 10.5 kcal/mol when a GVB calculation is employed (GVB(2)/6-31G*//3-21G, Table IV). For reasons pointed out above, this GVB value is probably too low. The transition state has C_1 symmetry and is characterized by rather a long O–O bond and a forming C–O bond (1.821 and 2.165 Å). The barrier calculated for the closure of **1b** to **2b**, via **TS1b-2b** in Figure 1, is only 10.4 kcal/mol by MP2/6-31G* and drops to 3.3 kcal/mol with the GVB(2)/6-31G*//3-21G method. Thus, the calculations indicate that **1b** should close to the dioxirane more readily than **1a**. At the same time a consideration of the calculated HOMO energies of **1a** (−11.94 eV) and **1b** (−13.90 eV) indicates that **1a** should be more reactive in a $4\pi + 2\pi$ cycloaddition.[3] While the experimental work presented here is not concerned with the chemistry of **1a**, these calculations do provide a rationalization for the different chemistry observed in the ozonolysis of ethylene as compared to that of tetrafluoroethylene.

The barrier for the conversion of acetaldehyde oxide to methyldioxirane is estimated to be about 16 kcal/mol.[4] The 33.6 kcal/mol barrier calculated at the MP2/6-31G* level (Table V) for **1a** to **2a** is considerably higher, while the barrier at GVB-(2)/6-31G* level (10.5 kcal/mol) is lower. A calculation of the barrier at the MP4SDQ/6-31G* level and optimizing geometries at that level[23] yields a value of 22.8 kcal/mol.

Although we feel that the species transferring oxygen in the $^3CF_2 + O_2$ system is **2b**, we cannot tell if this compound results directly from the reaction between CF_2 and O_2 or is produced via the intermediacy of **1b**. There is a precedent in the literature for the reaction of carbenes with oxygen to form carbonyl oxides and subsequently dioxiranes. Thus, when phenylchlorocarbene is reacted with O_2 in an argon matrix at 35 K, IR bands attributed to the corresponding carbonyl oxide are observed.[33] Since subsequent photolysis of the matrix is reported to generate the phenylchlorodioxirane, this system constitutes an example of dioxirane formation via the carbonyl oxide. Several other investigations of the reaction of carbenes with oxygen in low-temperature matrices also report initial formation of a carbonyl oxide.[34,35] However, in our experiments, the barrier to ring closure in **1b** is low enough that even if the carbonyl oxide were formed initially in the reaction of $^3CF_2$ with O_2, rapid collapse to the dioxirane would ensue.

Table VI shows the transition-state energies calculated for the transfer of oxygen to ethylene from both **2a** and **2b** (via **TS2a-Et** and **TS2b-Et**). An examination of this data reveals that **2b**, with a barrier of only 7.2 kcal/mol, is far more likely to transfer its oxygen than is **2a** (E_a = 51.1 kcal/mol). In both cases, the transition states are characterized by rather long incipient epoxide bonds and a lengthening of the O–O bond in the dioxirane (see for example **TS2b-Et** in Figure 1) and thus may be predicted to be too unstable for the same reasons that **1a** is underestimated. It should be pointed out that the geometries are calculated at the 3-21G level and therefore may be somewhat poorly described due to a limited basis set (no polarization functions) and a poor description of the wave function (single configurational). Nonetheless, the large difference in barriers to oxygen transfer from **2a** and **2b** to ethylene leads us to conclude that O transfer from **2b** will remain the favored pathway when geometries are calculated by more accurate methods.

Cremer and Buck[36] have recently calculated a barrier of 4.7 kcal/mol for the transfer of oxygen from *carbonyl oxide* **1a** to ethylene to form the epoxide (our value of 51.1 kcal/mol is for transfer from the dioxirane). The significant difference between **TS2a-Et** and the transition state calculated by Cremer is the fact that the geometry of the former indicates that it has a dioxirane precursor while the latter arises from the carbonyl oxide. Our calculated energy difference between **1a** and **TS2a-Et** is 10.2 kcal/mol (51.1, Table VI minus 40.9, Table III).

Conclusions

These investigations demonstrate that the reaction of oxygen with $^3CF_2$ generates an intermediate, perhaps the dioxirane, which acts as an oxygen transfer reagent to convert olefins to epoxides stereospecifically.

Experimental Section

Carbon Atom Reactions. The carbon atom reactor is modeled after that reported by Skell, Wescott, Golstein, and Engel.[37] Carbon is vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and cocondensed with reactants at 77 K under vacuum.

Reaction of Carbon Vapor with Oxygen in the Presence of Added Alkenes. Oxygen (1.25 mmol) and the appropriate alkene (25 mmol) were allowed to mix in a vacuum line for 0.5 h. The mixture was allowed to cocondense with carbon vapor (4.0–6.2 mmol) at 77 K. At the conclusion of the reaction, volatile products were pumped out and analyzed for carbonyl compounds and epoxides by GC on a 6-ft Porapak Q (80–100 mesh) column and gave the yields in Table I. In all cases, retention times and infrared spectra were identical with those of authentic samples.

Reaction of Carbon Vapor with Tetrafluoromethane in the Presence of Oxygen and Alkenes. In a typical reaction, CF_4 (25 mmol), oxygen (2.5 mmol), and alkene (15 mmol) were allowed to mix for 0.5 h in the vacuum line. The gas mixture was allowed to condense with carbon vapor (5.1–5.9 mmol) as above. At the conclusion of the reaction, volatile products were pumped out and analyzed for carbonyl compounds and epoxides by GC–MS on a 6-ft Porapak Q (80–100 mesh) column and gave the yields in Table I. In all cases, retention times and mass spectra were identical with those of authentic samples.

Reaction of Carbon Vapor with Perfluoroisobutane in the Presence of Oxygen and Ethylene. Perfluoroisobutane (34.6 mmol), oxygen (3.45 mmol), and ethylene (20.7 mmol) were allowed to mix for 0.5 h in the vacuum line. The gas mixture was allowed to condense with carbon vapor (25 mmol) as above. At the conclusion of the reaction, volatile products were pumped out and analyzed for acetaldehyde and ethylene oxide by IR spectroscopy, by GC, and GC–MS on a 6-ft Porapak Q (80–100 mesh) column. In no analysis could ethylene oxide or acetaldehyde be detected.

Acknowledgment. M.R. and P.B.S. gratefully acknowledge support of this research by the National Science Foundation (Grant CHE-8401198). M.L.M. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. We thank the Auburn University Computation Center and Mass Spectrometry Facility for generous allotments of time.

---

(33) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517.

(34) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213.

(35) Chapman, O. L.; Hess, T. C. *J. Am. Chem. Soc.* **1984**, *106*. 1842.

(36) Cremer, D.; Bock, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 3375.

(37) Skell, P. S.; Wescott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.