8990 *J. Am. Chem. Soc.* **2000,** *122,* 8990−8997

Theoretical Investigation of Reaction Mechanisms for Carboxylic Acid Formation in the Atmosphere

P. Aplincourt and M. F. Ruiz-López*

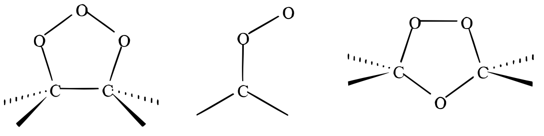
Contribution from the Laboratoire de Chimie Théorique, UMR CNRS-UHP No. 7565,[‡] Université Henri Poincaré−Nancy I, BP 239, 54506 Vandoeuvre-les-Nancy Cedex, France

Received February 29, 2000. Revised Manuscript Received July 17, 2000

Abstract: Theoretical calculations have been carried out to investigate the mechanism of several chemical reactions that may explain the formation of formic acid in the atmosphere. All the envisaged processes involve the so-called Criegee intermediate, H_2COO, which is generated in the course of the ozonolysis reaction. We focus on isomerization of carbonyl oxide through bimolecular reactions with H_2CO, H_2O, SO_2, and CO_2. The results are compared with those obtained for unimolecular isomerization mechanisms previously reported in the literature. In the bimolecular processes, there is always formation of an intermediate adduct, the stability of which increases in the order CO_2 (−24.5 kcal/mol) < SO_2 (−43.1 kcal/mol) < H_2O (−45 kcal/mol) < H_2CO (−49 kcal/mol) (values at the CCSD(T) level with zero-point energy correction at the B3LYP level). Note that the formation of this adduct may or may not be preceded by the formation of a stable complex. Afterward, the adduct decomposes to form the final products according to a one-step (H_2O, SO_2, CO_2) or a stepwise mechanisms (H_2CO). The whole $H_2COO + M \rightarrow HCOOH + M$ reaction energy is −118.3 kcal/mol at the CCSD(T) level. The computed results for activation energies suggest that the reactions with H_2O, H_2CO, and SO_2 are likely to occur, whereas that with CO_2 is unfavorable. Because of the high concentration of H_2O in atmospheric conditions, the reaction with this molecule should play a major role.

1. Introduction

The ozonolysis reaction is the only known source of carboxylic acids in the atmosphere. However, the mechanisms involved are unclear. In general, it is assumed that the first step of the ozonolysis reaction mechanism in the gas phase is the same as that in solution. According to Criegee,[1] ozone attacks CC double bonds to form primary ozonides (1,2,3-trioxolanes), which then decompose to yield carbonyl oxides and carbonyl compounds (see typical structure in eq 1). In solution, carbonyl oxides recombine with carbonyl compounds to yield secondary ozonides (1,2,4-trioxolanes), which are much more stable than primary ozonides. In the gas phase, the latter reaction is not the most important one,[2,3] and carbonyl oxides are supposed to undergo unimolecular reactions (isomerizations, decomposition, etc.)[3−11] or reactions with other compounds.[1,12−15]


(1)

Primary ozonide **1a** Carbonyl oxide **1b** Secondary ozonide (SO) **1c**

Carbonyl oxides are 1,3-dipoles exhibiting remarkable oxidation properties. Many experimental studies have been devoted to this class of compounds[9] that are also involved in biochemical oxidations[16] and environmental processes.[17] One should note in particular that carbonyl oxides are a source of OH and HO_2 radicals,[4] which play a key role in the chemistry of the troposphere.

Carbonyl oxides have also been studied theoretically.[6,7,18−45] Because of their very weak stability, theoretical calculations

---

* To whom correspondence should be addressed. Phone: (33) 3 83 91 25 27. Fax: (33) 3 83 91 25 30. E-mail: Manuel.Ruiz@lctn.u-nancy.fr.

[‡] Part of the Institut Nancéien de Chimie Moléculaire.

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

(2) Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1977**, *99*, 5430.

(3) Martinez, R. I.; Herron, J. T. *J. Phys. Chem.* **1988**, *92*, 4644.

(4) Mihelcic, D.; Heitlinger, M.; Kley, D.; Müsgen, P.; Volz-Thomas, A. *Chem. Phys. Lett.* **1999**, *301*, 559.

(5) Paulson, S. E.; Fenske, J. D.; Sen, A. D.; Callahan, T. W. *J. Phys. Chem. A* **1999**, *103*, 2050.

(6) Gutbrod, R.; Kraka, E.; Schindler, R. N.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7330.

(7) Olzmann, M.; Kraka, E.; Cremer, D.; Gutbrod, R.; Andersson, S. *J. Phys. Chem. A* **1997**, *101*, 9421.

(8) Atkinson, R.; Aschmann, S. M. *Environ. Sci. Technol.* **1993**, *27*, 1357.

(9) Iesce, M. R.; Cermola, F.; Scarpati, R. *J. Org. Chem.* **1996**, *61*, 8677. For a review, see: Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335.

(10) Sander, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 988.

(11) Story, P. S.; Burgess, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 5726; **1968**, *90*, 1094.

(12) Neeb, P.; Horie, O.; Moortgat, G. K. *Chem. Phys. Lett.* **1995**, *246*, 150.

(13) Hatakeyama, S.; Kobayashi, H.; Lin, Z.-Y.; Takagi, H.; Akimoto, H. *J. Phys. Chem.*, **1986**, *90*, 4131.

(14) Hatakeyama, S.; Kobayashi, H.; Akimoto, H. *J. Phys. Chem.* **1984**, *88*, 4736.

(15) Hatakeyama, S.; Bandow, H.; Okuda, M.; Akimoto, H. *J. Phys. Chem.* **1981**, *85*, 2249.

(16) (a) Walsh, C. T.; Chen, Y. C. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 333. (b) Dix, T. A.; Benkovic, S. J. *Acc. Chem. Res.* **1988**, *21*, 101.

(17) Kumar, S.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1040.

(18) Anglada, J. M.; Crehuet, R.; Bofill, J. M. *Chem. Eur. J.* **1999**, *5*, 1809.

(19) Cremer, D.; Kraka, E.; Szalay, P. G. *Chem. Phys. Lett.* **1998**, *292*, 97.

(20) Anglada, J. M.; Bofill, J. M.; Olivella, S.; Solé, A. *J. Phys. Chem. A* **1998**, *102*, 3398.

(21) Anglada, J. M.; Bofill, J. M. *J. Org. Chem.* **1997**, *62*, 2720.

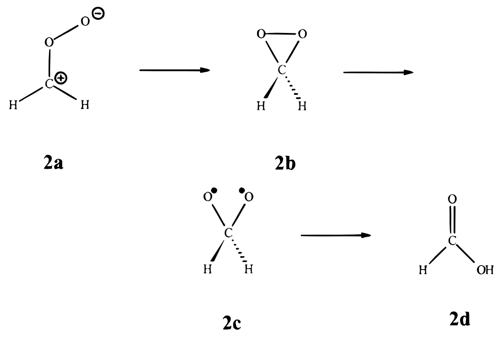
(22) Gutbrod, R.; Schindler, R. N.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1996**, *252*, 221.

(23) Anglada, J. M.; Bofill, J. M.; Olivella, S.; Solé, A. *J. Am. Chem. Soc.* **1996**, *118*, 4636.

10.1021/ja000731z CCC: $19.00

are very useful, especially in determining geometric and electronic structures of this class of compounds.

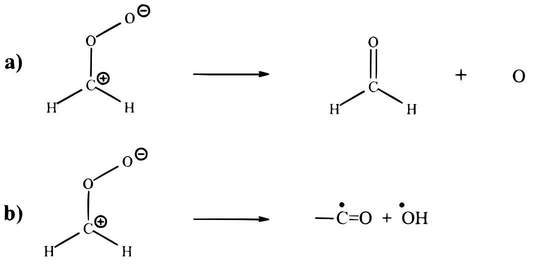
On the basis of experimental results for the gas-phase ozone–ethene reaction, Herron and Huie[2] proposed that the fate of carbonyl oxide was determined by unimolecular loss processes:



(2)

The rearrangement of carbonyl oxides into dioxiranes and methylenebis(oxy) compounds has been reviewed.[46] Dioxirane (**2b**) may also dissociate into CO_2 and H_2 or react with other compounds present in the media. Dioxiranes are substantially more stable than the corresponding carbonyl oxides, and some derivatives have been isolated.[47] Their chemistry has been studied extensively experimentally by Murray and co-workers[48] and theoretically by Bach and co-workers.[27,49] In particular, dioxiranes, like carbonyl oxides, are excellent epoxidation agents.[50,51]

Extension of the work by Herron and Huie to other alkenes,[52] however, did not lead to equivalent conclusions, i.e., total conversion of carbonyl oxide to an acid or an ester according to **2**. Further work[53] confirmed the role of two other processes, one yielding an oxygen atom (eq 3a) and another yielding hydroxyl and formyl radicals (eq 3b).



(3)

Apart from the unimolecular reaction described above, other atmospheric processes have been claimed to explain carboxylic acid formation. Hatakeyama et al.[15] showed experimental evidence that the reaction of carbonyl oxide with water vapor leads to an isomerization mechanism of carbonyl oxide into formic acid. The reaction of carbonyl oxides with SO_2 has also been invoked.[13,14] This reaction was experimentally investigated in the 1980s due to its possible contribution to acid rain through H_2SO_4 formation.[54] Thus, the experimental results suggested the formation of an intermediate adduct that either decomposed to yield formic acid (regenerating SO_2) or reacted with another SO_2 molecule to yield SO_3. Further combination of SO_3 with water led to sulfuric acid. Hawkins et al.[55] studied a photolytic mechanism in which secondary ozonides isomerize to yield hydroxymethyl formate, $HOCH_2OCHO$ (hereafter abbreviated HMF), which then decomposes to formic acid and formaldehyde.

Some theoretical work on carboxylic acid formation has been published. Basically, most theoretical calculations have been devoted to study the isomerization and dissociation reactions (eqs 2 and 3),[6,7,18−26] although direct decomposition of secondary ozonide into formic acid and formaldehyde has also been discussed.[44] But a deeper understanding of carboxylic acid formation in atmospheric conditions deserves further investigation. In the present work, the attention is focused on bimolecular processes of the type $H_2COO + M \rightarrow HCOOH + M$, where M is a molecule that formally behaves as an ancillary species assisting the isomerization. We have examined the reactions for $M = H_2O$, SO_2, CO_2, and H_2CO, several mechanisms being possible in general for each molecule. First of all, calculations for unimolecular processes previously done are summarized, although for comparative purposes, we have recomputed the reaction mechanisms and activation energies at the level used in this paper. Then, calculations for the above-mentioned processes using correlated ab initio and density functional techniques are detailed.

---

(24) Bach, R. D.; Andrés, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207.

(25) Cremer, D.; Schmidt, T.; Gauss, J.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed. Eng.* **1988**, *27*, 427.

(26) Karlström, G.; Roos, B. O. *Chem. Phys. Lett.* **1981**, *79*, 416.

(27) Baboul, A. G.; Schlegel, H. B.; Glukhovtsev, M. N.; Bach, R. D. *J. Comput. Chem.* **1998**, *19*, 1353.

(28) Selçuki, C.; Aviyente, V. *Chem. Phys. Lett.* **1998**, *288*, 669.

(29) Bernhardsson, A.; Lindh, R.; Karlström, G.; Roos, B. O. *Chem. Phys. Lett.* **1996**, *251*, 141.

(30) Cremer, D.; Gauss, J.; Kraka, E.; Stanton, J. F.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *209*, 547.

(31) Dewar, M. J. S.; Hwang, J. C.; Kuhn, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 735.

(32) Cremer, D.; Schmidt, T.; Sander, W.; Bischof, P. *J. Org. Chem.* **1989**, *54*, 2515.

(33) Gauss, J.; Cremer, D. *Chem. Phys. Lett.* **1987**, *133*, 420.

(34) Yamaguchi, K.; Yabushita, S.; Fueno, T.; Kato, S.; Morokuma, K.; Iwata, S. *Chem. Phys. Lett.* **1980**, *71*, 563.

(35) Karlström, G.; Engström, S.; Jönsson, B. *Chem. Phys. Lett.* **1979**, *67*, 343.

(36) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180.

(37) Hull, L. A. *J. Org. Chem.* **1978**, *43*, 2780.

(38) Hiberty, P. C. *J. Am. Chem. Soc.* **1976**, *98*, 6088.

(39) Wadt, W. R.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1975**, *97*, 3004.

(40) Ha, T.-K.; Kühne, H.; Vaccani, S.; Günthard, H. H. *Chem. Phys. Lett.* **1974**, *24*, 172.

(41) Ponec, R.; Yuzhakov, G.; Haas, Y.; Samuni, U. *J. Org. Chem.* **1997**, *62*, 2720.

(42) Cremer, D.; Kraka, E.; McKee, M. L.; Radhakrishnan, T. P. *Chem. Phys. Lett.* **1991**, *187*, 491.

(43) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3620, 3627, 3633.

(44) Selçuki, C.; Aviyente, V.; Aplincourt, P.; Ruiz-Lopez, M. F. Submitted for publication.

(45) Aplincourt, P.; Ruiz-Lopez, M. F. *J. Phys. Chem. A* **2000**, *104*, 380.

(46) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, (a) 1978; Vol. I; (b) 1982; Vol. II.

(47) (a) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem.* **1988**, *53*, 3890. (b) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(48) For a review, see: Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187.

(49) (a) Bach, R. D.; Glukhovtsev, M. N.; Canepa, C. *J. Am. Chem. Soc.* **1998**, *120*, 775. (b) Bach, R. D.; Glukhovtsev, M. N.; Gonzalez, C.; Marquez, M.; Estevez, C. M.; Baboul, A. G.; Schlegel, H. B. *J. Phys. Chem. A* **1997**, *101*, 6092. (c) Bach, R. D.; Owensby, A. L.; Andrés, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7031.

(50) Kwart, H.; Hoffman, D. M. *J. Org. Chem.* **1966**, *31*, 419.

(51) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* **1979**, *101*, 1282.

(52) Martinez, R. I.; Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3807.

(53) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P.; Hurley, M. D. *J. Phys. Chem.* **1987**, *91*, 941.

(54) Calvert, J. G.; Lazrus, A.; Kok, G. L.; Heikes, B. G.; Walega, J. G.; Lind, J.; Cantrell, C. A. *Nature* **1985**, *317*, 27.

(55) Hawkins, M.; Kohlmiller, C. K.; Andrews, L. *J. Phys. Chem.* **1982**, *86*, 3154.

Table 1. Theoretical Data for Activation and Reaction Energies (in kcal/mol) of Some Unimolecular Reactions Involving Carbonyl Oxide[a]

reactant	product	activation energy	reaction energy	ref
H_2COO (**2a**)	$H_2CO + O(^1D)$	32.4	32.4	23
	HCO + OH	34.0	−7.8	6
	dioxirane (**2b**)	19.2	−25.6	30
		24.0	−28.5	23
		19.1	−28.6	24
		20.1	−28.0	19
		19.9	**−26.2**	**this work**
dioxirane (**2b**)	dioxymethane (**2c**)	21.4	5.8	20
		19.9	**7.5**	**this work**
	$CO_2 + H_2$	**26.9**	**−98.9**	**this work**
dioxymethane (**2c**)	$CO_2 + H_2$	3.2	−105.2	20
		4.3	−116.9	19
		2.3	**−106.4**	**this work**
	formic acid (**2d**)	2.8	−95.7	19
		6.5	**−99.5**	**this work**

[a] Structures are drawn in Figure 1.

A final comment can be added. The reactions studied here appear to be the best candidates to explain carboxylic acid formation during the ozonolysis reaction in the atmosphere. In addition, some of them play a crucial role in oxidation processes in biological and solution chemistry. Therefore, the theoretical analysis of their mechanisms and the evaluation of the corresponding energetics should be of wide interest.

2. Calculations

We study here the reactions for the simplest compounds, i.e., substituents effects are not taken into account: the initial olefin is assumed to be ethylene and the final product formic acid. The computational level has been chosen as a compromise between accuracy and computational cost. Of course, our choice takes into account the conclusions reached in previous studies on similar systems. Thus, the geometry optimizations and transition states location have been done using density functional methods. In particular, we use the B3LYP functional.[56,57] Afterward, single-point energy calculations are carried out using the more highly correlated ab initio level CCSD(T).[58] Basis sets are 6-31G(d,p)[59a] for DFT-B3LYP and 6-311G(d,p)[59b,60] for CCSD(T). A set of diffuse orbitals has been added on the sulfur atom in both B3LYP and CCSD(T) calculations.

Density functional theory (DFT) has been widely employed by different authors in the context of the ozonolysis reaction.[6,7,19,45] Gutbrod et al.[22] have shown that the optimized geometry of carbonyl oxide at the B3LYP level reproduces very well the values obtained with the more costly CCSD(T) method. They used such an approach to study H-transfer reactions that resemble some of the processes considered in our work. Recently, Cremer et al.[19] studied some of the unimolecular reactions presented below, making a comparison between various computational levels. They considered, in particular, the isomerization of carbonyl oxide into dioxirane, then into dioxymethane. The results of B3LYP calculations for the transition structure geometries were shown to be reasonably good compared to those obtained by sophisticated ab initio calculations. Moreover, Pérez-Casany et al.[61] investigated the reaction of propene with the nitrate radical and concluded that deviations of the B3LYP geometries from the CASSCF ones are small enough to consider that the former level is a good compromise between quality and computational cost for the study of our systems.

One should note that correlated calculations at the MP2 level do not necessarily constitute a better approach than DFT for the systems considered here. For instance, the MP2 method overestimates substantially the diradical character of carbonyl oxide, whereas DFT results appear to be consistent with high-level correlated computations.[30] Accordingly, the OO and CO bond lengths at the B3LYP level (1.343, 1.266 Å)[22] are comparable to values obtained using CCSD(T)/TZ+2P high-level calculations (1.355, 1.276 Å),[22] whereas MP2 results are considerably different (1.293, 1.297 Å).[30]

Frequency calculations were done in order to verify the nature of the stationary points (minimum or saddle point). For all transition states, we have verified that the Hessian matrixes lead to only one imaginary frequency. Zero-point energy (ZPE) corrections have been obtained using frequencies scaled by a factor of 0.963. All of our calculations have been performed with the Gaussian94 package.[62]

3. Results

First, we briefly summarize precedent theoretical results for unimolecular processes. Then, we present for the first time a series of bimolecular mechanisms for carbonyl oxide isomerization. Unless otherwise quoted, the energies used in this section correspond to CCSD/6-311G(d,p) values for B3LYP/6-31G(d,p)-optimized geometries with ZPE corrections at the latter level.

A. Unimolecular Isomerization. Let us first summarize the results for the unimolecular isomerization process 2. The corresponding optimized structures are given in Figure 1. Direct conversion of **2a** or **2b** into **2d** was attempted, but we did not succeed in finding a transition structure, so one may conclude that conversion of carbonyl oxide to formic acid by unimolecular isomerization processes can be envisaged only through the three-step process shown in eq 2.

In Table 1, we have summarized the most interesting results from the literature as well as those obtained in the present work. We include data for other unimolecular reactions that could be of relevance in our study. In particular, dissociation of **A** into formaldehyde and atomic oxygen (reaction 3a) must be taken into account since one may expect a fast recombination of the species to yield either **2b** or **2c**. However, dissociation through singlet states is substantially endothermic[23] and is unlikely to occur. It should be noted that when triplet states for carbonyl oxide and oxygen atom are considered,[23] the reaction is, in contrast, quite exothermic, displaying a very small barrier. But due to the low efficiency of intersystem crossing with the singlet state, this channel is not operational.

Cyclization of **2a** to dioxirane **2b** has been most widely studied.[19,23−26,30] It requires an activation energy of about 20 kcal/mol (depending on the method). Anglada et al.[20] investigated the ring opening **2b** → **2c** and dissociation of **2c** into CO_2 and H_2. The ground-state activation energies were estimated to be 21.4 and 3.2 kcal/mol, respectively, and processes through the low-lying electronic states were examined. Cremer et al.[19] have examined decomposition of **2c**, in particular the isomerization process **2c** → **2d**. The authors have shown that decomposition reactions of **2c** (isomerization into formic acid and dissociation into CO_2 and H_2) should be very fast because

---

[56] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[57] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

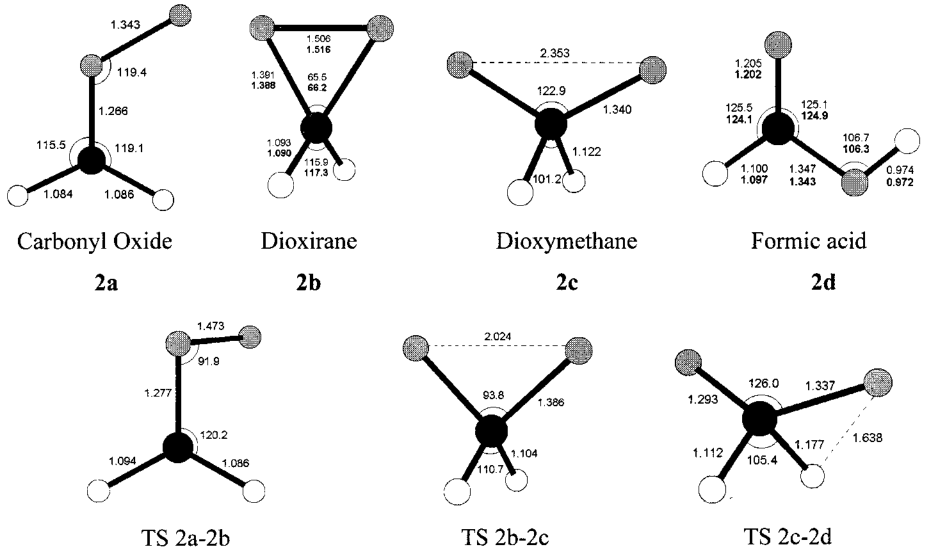
[58] For this method, see, for example: Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan: New York, 1986; pp 285−296.

[59] (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[60] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

[61] Pérez-Casany, M. P.; Nebot-Gil, I.; Sánchez-Marín, J. *J. Phys. Chem. A* **2000**, *104*, 6277.

[62] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian94*, Revision B.3, Gaussian Inc.: Pittsburgh, PA, 1995.



Carbonyl Oxide **2a** Dioxirane **2b** Dioxymethane **2c** Formic acid **2d**

TS 2a-2b TS 2b-2c TS 2c-2d

Figure 1. B3LYP-computed structures for the unimolecular reactions of carbonyl oxide (angstroms and degrees). Carbon, oxygen, and hydrogen atoms are respectively in black, gray, and white. We have reported, in bold, experimental values when available. See relative energies in Table 1.

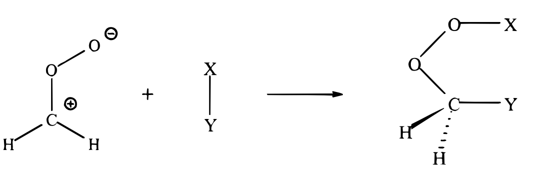
Table 2. Relative Energies (in kcal/mol) Computed for the Bimolecular Reaction of Carbonyl Oxide and Water[a]

H_2O	B3LYP	CCSD(T)	ΔZPE
	HMHP Formation		
$H_2COO + H_2O$	0.0	0.0	0.0
complex	−11.4	−9.7	+ 2.5
TS a	−5.0	−0.5	+ 2.8
HMHP	−48.5	−50.0	+ 5.0
	HCOOH Formation		
HMHP + H_2O	0.0	0.0	0.0
TS b	27.3	38.0	−2.7
HCOOH + $2H_2O$	−68.2	−70.0	−3.3

[a] Structures are drawn in Figure 2.

of the small activation barriers associated with them (see Table 1). In addition, as the reaction products are much more stable than dioxymethane, backward reactions are impossible. Therefore, the probability of detecting dioxymethane **2c** in the gas phase is particularly low.

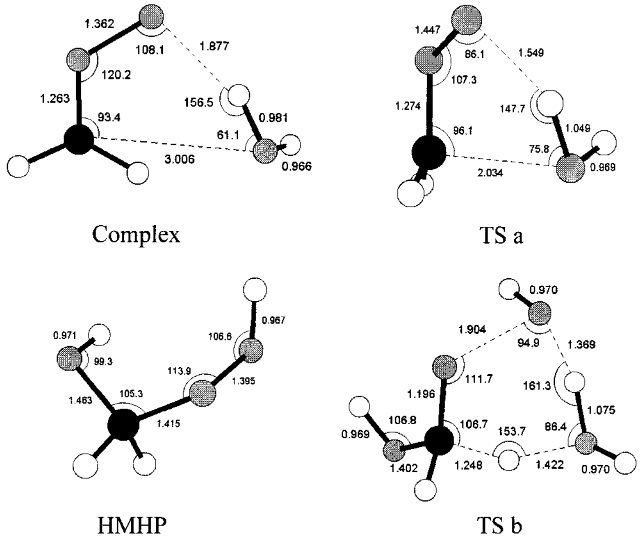
B. Bimolecular Processes. The global scheme for these reactions is $H_2COO + M \rightarrow HCOOH + M$, M being a molecular species that may be considered as an isomerization catalyst. However, the reactions always involve the initial break of a chemical bond in M. Assuming M = X—Y, one has



(4)

For X=Y double bonds, the reaction leads to a cyclic adduct. Decomposition of the adduct to form HCOOH allows M to be regenerated, the actual mechanism depending on the nature of the ancillary molecule. We now examine a few cases that could exhibit special importance under atmospheric conditions. We consider the reactions with H_2O, SO_2, CO_2, and H_2CO. In all these cases, Y is an oxygen atom. All the compounds involved in these reactions are pictured in Figures 2−5. Relative energies are summarized in Tables 2−5.

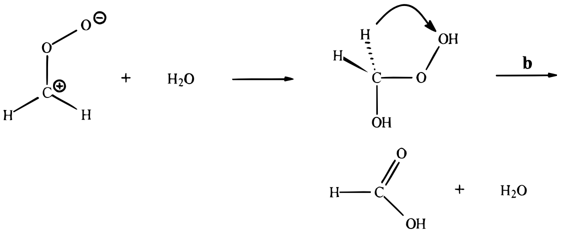
Reaction with H_2O. The results for this reaction are summarized in Table 2 and Figure 2. The following mechanism was proposed by Hatakeyama et al.:[15]



Complex TS a

HMHP TS b

Figure 2. B3LYP-computed structures for the bimolecular reaction of carbonyl oxide and water (angstroms and degrees). Carbon, oxygen, and hydrogen atoms are respectively in black, gray, and white. See relative energies in Table 2.



(5)

The authors noted that use of marked $H_2{}^{18}O$ produced ^{18}O-labeled formic acid, $HC^{18}OOH$, $HCO^{18}OH$, and H_2O. According to reaction 5, only $HCO^{18}OH$ should be obtained, but rapid proton exchange between two acid molecules or between the acid and water would lead to the formation of acid labeled on a carbonyl oxygen atom.

The first step of this mechanism is expected to be easy due to the high reactivity of carbonyl oxide. This is, indeed, found by our computations. Initially there is formation of a complex which is 7.2 kcal/mol more stable than the separate reactants. The reaction proceeds through an activation barrier of 9.5 kcal/

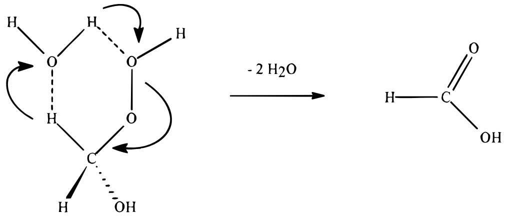
Table 3. Relative Energies (in kcal/mol) Computed for the Bimolecular Reaction of Carbonyl Oxide and SO_2[a]

SO₂	B3LYP	CCSD(T)	ΔZPE
$H_2COO + SO_2$	0.0	0.0	0.0
cyclic adduct	−39.0	−46.9	+ 3.8
TS	−11.4	−18.3	−0.2
$HCOOH + SO_2$	−116.7	−120.0	+ 1.7

[a] Structures are drawn in Figure 3.

mol (TS a) to yield the adduct hydroxymethyl hydroperoxyl, $HOCH_2OOH$ (hereafter abbreviated HMHP), which is substantially more stable than the separate reactants (−45 kcal/mol).

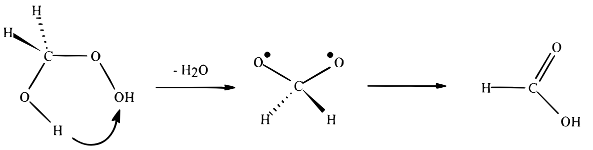
In contrast to the first step, the second one (eq 5b) must display a substantial activation energy. One may get an order of magnitude by considering the theoretical calculations reported by us for a close reaction in which hydroperoxymethylformate ($HCO-O-H_2C-OOH$, or HPMF) leads to formic acid anhydride and water[45] (note that the difference between HPMF and the intermediate in eq 5 is the substitution of HO− by the HCO−O− group). The predicted barrier was quite large, 45.6 kcal/mol, obtained using MP4/6-311G(d,p)//B3LYP/6-31G(d,p) computations, including zero-point energy corrections.[45] We also showed in that paper that the process may be assisted by an ancillary molecule bearing an OH group, the catalytic effect being of the order of 10 kcal/mol. In the present case, one could postulate the following:



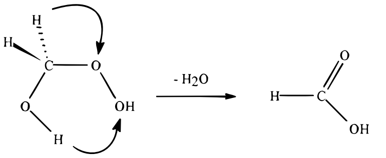
(6)

We have located the corresponding transition structure which is described in Figure 2 (TS b). Note in particular that the OO bond being broken is substantially elongated with respect to that in HMHP. The activation barrier (35.3 kcal/mol) is very close to that obtained for the process HPMF + HCOOH → FAA + H_2O.[45]

We have searched for other possible dehydration mechanisms. The following cases have been envisaged:

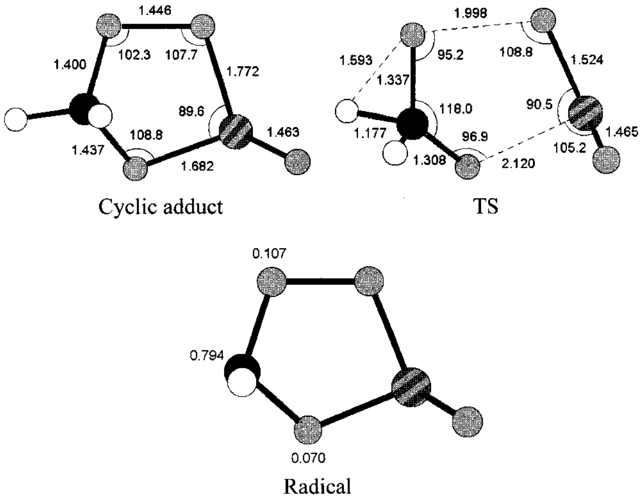


(7)



(8)

Computations show that eq 7 is unlikely: the first step is endothermic by about 30 kcal/mol, and attempts to locate a transition structure were unsuccessful. Similarly, a transition structure for eq 8 could not be found.

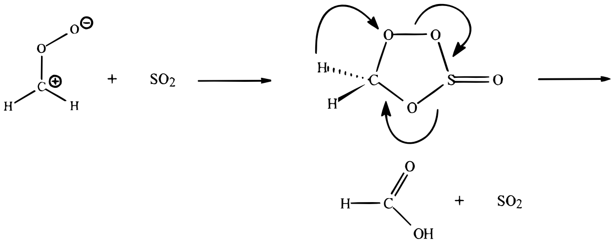


Cyclic adduct TS

Radical

Figure 3. B3LYP-computed structures for the bimolecular reaction of carbonyl oxide and SO_2 (angstroms and degrees). Carbon, oxygen, and hydrogen atoms are respectively in black, gray, and white. The sulfur atom is represented by an hatched atom. See relative energies in Table 3.

Reaction with SO_2. The results for this reaction are summarized in Table 3 and Figure 3. As explained in the Introduction, Hatakeyama et al.[13,14] have investigated the reaction of carbonyl oxide with SO_2 and showed that carboxylic acids may be formed. The reaction involves an intermediate adduct that was identified to be a cyclic species already described by Martinez and Herron.[63−65] The reaction mechanism proposed was



(9)

Computations lead to a highly exothermic, barrierless process for the addition step (−43.1 kcal/mol), whereas the barrier for the second step is 24.6 kcal/mol.

As another possible mechanism for the second step, we have considered H-transfer to the O atom in the opposite side of the ring, i.e., that bonded simultaneously to both C and S. Attempts to locate the corresponding TS at the B3LYP level were not successful. A structure was located, however, in preliminary calculations at the simple HF/3-21+G level, and further single-point energy calculations at the CCSD(T)/6-311G(d,p) level showed that this structure is less stable than the TS involved in eq 9 by more than 10 kcal/mol. This result may be interpreted by considering the electronic properties of the radical drawn in Figure 3. It represents the species derived from the cyclic intermediate after abstraction of an H atom. The spin density is higher on the upper O atom, and hydrogen transfer to it is expected to be favored.

Reaction with CO_2. The results for this reaction are summarized in Table 4 and Figure 4. Reactions between carbonyl oxides and carbon dioxide, which is a species present in high concentrations in the atmosphere, have not been

---

(63) Martinez, R. I.; Herron, J. T. *Environ. Sci. Health Part A* **1983**, *A18*, 739.

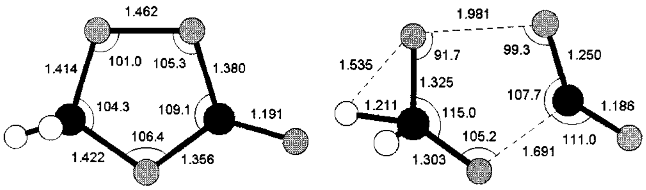
(64) Martinez, R. I.; Herron, J. T. *Environ. Sci. Health Part A* **1981** *A16*, 623.

(65) Martinez, R. I.; Herron, J. T. *Chem. Phys. Lett.* **1980**, *72*, 77.

Table 4. Relative Energies (in kcal/mol) Computed for the Bimolecular Reaction of Carbonyl Oxide and CO_2[a]

CO_2	B3LYP	CCSD(T)	ΔZPE
$H_2COO + CO_2$	0.0	0.0	0.0
cyclic adduct	−26.4	−28.7	+4.2
TS	15.5	19.4	−0.7
$HCOOH + CO_2$	−116.7	−120.0	+1.7

[a] Structures are drawn in Figure 4



Cyclic adduct TS

Figure 4. B3LYP-computed structures for the bimolecular reaction of carbonyl oxide and CO_2 (angstroms and degrees). Carbon, oxygen, and hydrogen atoms are respectively in black, gray, and white. See relative energies in Table 4.

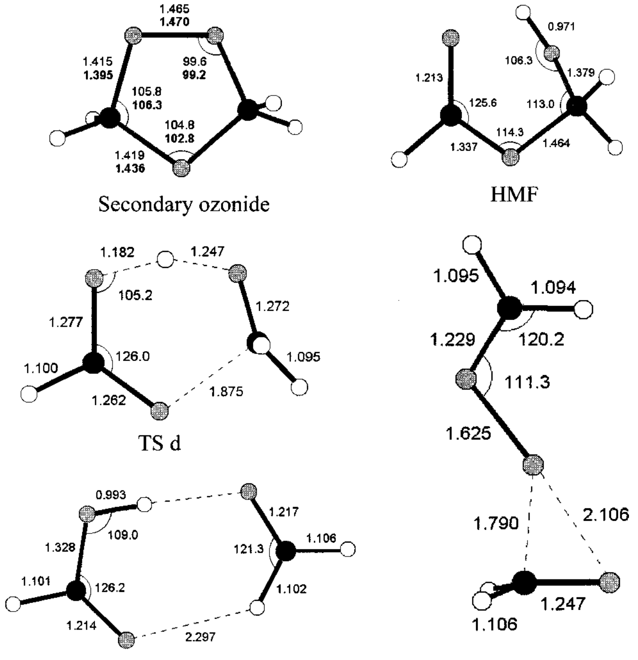
Table 5. Relative Energies (in kcal/mol) Computed for the Bimolecular Reaction of Carbonyl Oxide and H_2CO[a]

H_2CO	B3LYP	CCSD(T)	ΔZPE
	Reaction 12		
$H_2COO + H_2CO$	0.0	0.0	0.0
complex 1	−8.8	−7.5	+1.7
TS a	−8.4	−6.7	+2.1
secondary ozonide	−51.8	−55.0	+6.0
TS b	−29.9		+2.6
diradical	−34.0		+2.0
TS c	−27.1		−0.1
HMF	−130.1	−133.6	+6.1
TS d	−110.2	−108.3	+2.6
complex 2	−125.5	−130.0	+3.7
$HCOOH + H_2CO$	−116.7	−120.0	+ 1.7
	Reaction 13		
$H_2COO + H_2CO$	0.0	0.0	0.0
TS e	13.4	18.2	+ 1.1
dioxirane + H_2CO	−22.3	−27.0	+ 0.8
dioxirane	0.0	0.0	0.0
TS 2b-2c	24.6	20.9	−1.0
dioxymethane	4.1	10.0	−2.5
TS 2c-2d	7.6	15.8	−1.8
HCOOH	−94.4	−93.0	+ 0.9

[a] Structures are drawn in Figure 5; see Figure 1 and ref 45 for other geometries. See Table 6 for CASPT2 relative energies of TS a, diradical, and TS b.

previously studied. We have carried out calculations for a mechanism similar to that for SO_2 (see eq 9). The values obtained show that the formation of the cyclic adduct is, like for SO_2, exothermic and barrierless, although the reaction energy is now smaller (−24.5 kcal/mol). The activation barrier of the ring decomposition is now much higher (43.2 kcal/mol).

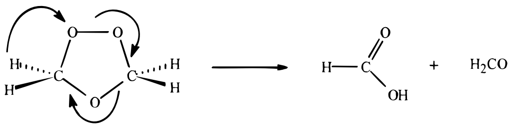
Reaction with H_2CO. All the results are gathered in Table 5 and Figure 5. Obviously, formation of secondary ozonide (see reaction 2) is the essential reaction between carbonyl oxides and aldehydes. It has been extensively studied,[36,39,41−43] and computations carried out at the CCSD(T) level,[45] equivalent to those employed here, show that formaldehyde and carbonyl oxide form initially a stable complex (−5.8 kcal/mol with respect to reactants) that evolves to secondary ozonide through a small transition barrier (1.2 kcal/mol). The ozonide is −49.0 kcal/mol more stable than the separate reactants.



Secondary ozonide HMF TS d Complex 2 TS e

Figure 5. B3LYP-computed structures for the bimolecular reaction of carbonyl oxide and H_2CO (angstroms and degrees). Carbon, oxygen, and hydrogen atoms are respectively in black, gray, and white. See relative energies in Table 5.

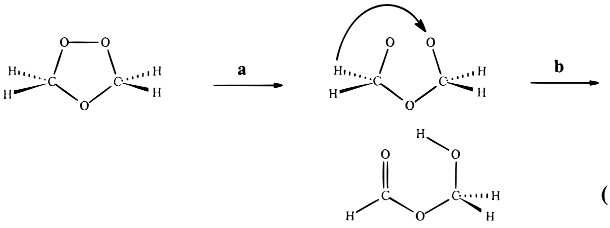
The secondary ozonide may then decompose to yield carboxylic acids and carbonyl compounds according to the following mechanism:



(10)

This process has been described theoretically before[44] and will not be considered here in detail. The activation barrier was estimated to be quite large, about 49 kcal/mol (MP4(SDQ)/6-31+G(d) calculation including ZPE corrections).

Here, we have examined other secondary ozonide decomposition processes yielding HCOOH. The first one involves the formation of the intermediate HMF. This species has been shown to play a role in formic acid anhydride formation in the atmosphere,[66,67] and its formation from secondary ozonide has also been described theoretically.[18,45] The proposed mechanism is



(11)

The activation barriers for eqs 11a and 11b were computed at the CASPT2 level, which is suitable for the study of diradicals. The relative energies at this level are given in Table 6. The

---

(66) Su, F.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1980**, *84*, 239.

(67) Kan, C. S.; Su, F.; Calvert, J. G.; Shaw, J. H. *J. Phys. Chem.* **1981**, *85*, 2359.

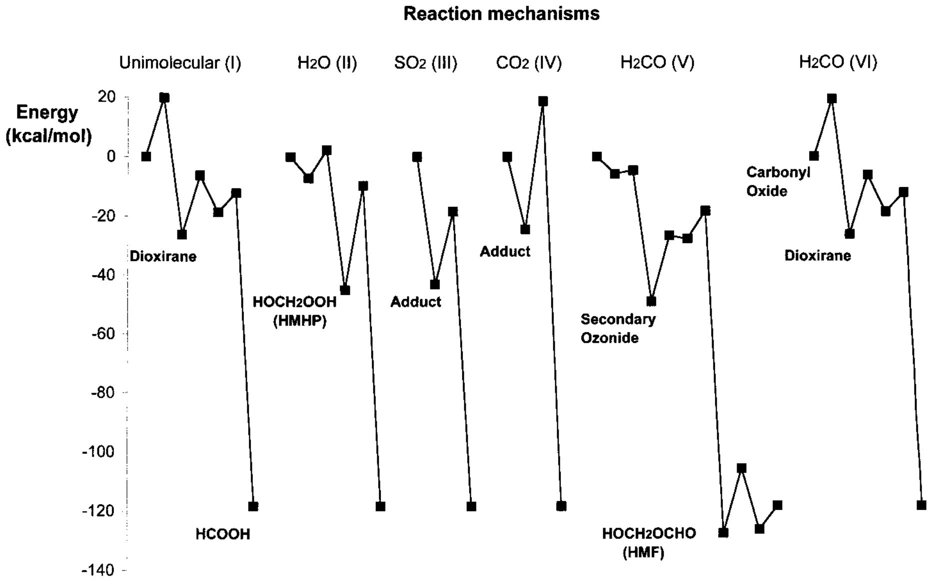


Figure 6. Relative energies (in kcal/mol) for all the isomerization processes (unimolecular and bimolecular) of carbonyl oxide (H_2COO) into formic acid (HCOOH). Relative energies are those computed at the CCSD(T) + ZPE level, except for the three radical structures between secondary ozonide and HMF in mechanism V. CASPT2 values + ZPE have been used in that case for the reasons explained in the text.

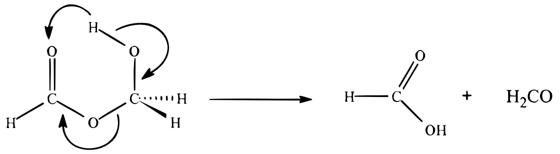
Table 6. Relative Energies (in kcal/mol) Computed for the Formation of HMF from Secondary Ozonide by a Stepwise Mechanism[a]

	active spaces[b]	
	(6,6)	(4,4)
secondary ozonide	0.0	
TS a	22.3	
diradical	21.2	0.0
TS b		9.4

[a] Energies are calculated at the CASPT2 level with the ANO basis set (contractions are (10s6p3d/3s2p1d) for C and O, (7s3p/2s1p) for H). Values are from ref 45. [b] In the (6,6) active space, six electrons are distributed in six MOs corresponding to the OO and CO bonding and antibonding orbitals. In the (4,4) active space, four electrons are distributed in four MOs corresponding to the OO and CH bonding and antibonding orbitals.

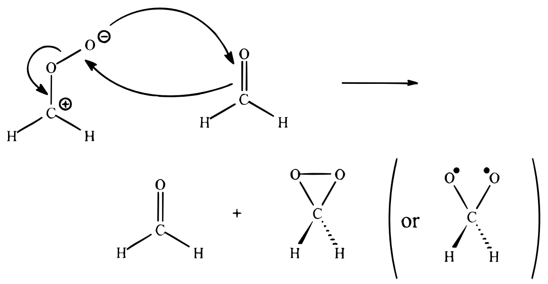
results show that the diradical lies in a shallow energy minimum. The global activation energy for HMF formation is given roughly by the difference between the energy of the TS for eq 10b and the energy of the secondary ozonide, about 30 kcal/mol. Note that CASPT2 calculations for eqs 11a and 11b were done using different active spaces, as required by the nature of the chemical bonds involved in the processes. The relative energy of HMF with respect to secondary ozonide is as large as −78.5 kcal/mol at the CCSD(T) level.[45]

The decomposition of HMF into formic acid and formaldehyde is studied here for the first time. We propose the mechanism depicted in eq 12. The results show that it is an endothermic process (9.2 kcal/mol) that needs an activation barrier of 21.8 kcal/mol.



(12)

Finally, we have envisaged another mechanism for the reaction of carbonyl oxide with formaldehyde in which the former behaves as an oxygen atom donor and the latter as an oxygen atom acceptor. The resulting O-donation process has some similarities with epoxidation reactions in which the terminal oxygen atom of a carbonyl oxide is transferred to a CC double bond.[49] According to it, one expects the formation of dioxirane or dioxymethane, as schematized in eq 13. Note that formic acid may then be formed through unimolecular isomerization, which is quite easy from dioxymethane, in particular.



(13)

After exploring the corresponding potential energy surfaces, only one TS has been located (see Figure 5), which corresponds to the process yielding dioxirane. The activation energy (19.3 kcal/mol) is slightly below the value for the unimolecular isomerization into dioxirane (19.9 kcal/mol).

C. Comparison of Reaction Mechanisms. To summarize the preceding calculations, the following mechanisms may be considered to explain acid formic formation:

(I) unimolecular isomerization:	process 2
(II) reaction with H_2O:	process 5a followed by 6
(III) reaction with SO_2:	process 9
(IV) reaction with CO_2:	process analogous to 9
(V) reaction with H_2CO:	formation of secondary ozonide followed by processes 11 and 12
(VI) reaction with H_2CO:	process 13

For comparison purposes, we plot in Figure 6 the energetics of the six reactions considered. For simplicity, we do not include the other possibilities that have been pointed out above and that are less favorable. One may make the following remarks:

(1) The mechanisms may be classified in two groups: those for which all the species along the reactant pathway remain below the reactants (mechanisms III and V), and those for which

some of the species lie above the reactants (mechanisms I, IV, and VI). The reaction with water (mechanism II) is an intermediate situation since the TS for adduct formation is very slightly less stable than the reactants (2.3 kcal/mol).

(2) The unimolecular mechanism I is expected to be important immediately after the formation of carbonyl oxide since it is well known that this species is generated in excited vibrationally states with an energy excess of 45−50 kcal/mol.[43] In that case, the barrier for conversion into dioxirane may be crossed readily. One may wonder whether molecular nitrogen, which is present in high concentrations in the atmosphere, could deactivate $[H_2COO]^\ddagger$ and quench the unimolecular decomposition process I. Indeed, the decomposition/stabilization ratio is highly dependent on the alkene considered and on the total pressure.[13,14] For ozone addition to ethene, about 60% of the H_2COO produced undergoes unimolecular reactions, whereas the other 40% gives rise to bimolecular reactions.[68]

(3) When carbonyl oxide is stabilized, bimolecular processes may take place, the reactions always starting with the formation of a quite stable adduct without significant (or moderated) activation energy. The adduct formation energy increases in the sense $CO_2 < SO_2 < H_2O < H_2CO$, although for the three latter cases, the energies are not very different.

(4) From the intermediate adducts formed in mechanism II, III, IV, or V, the transition-state energy for decomposition decreases in the sense $CO_2 > H_2O > SO_2 > H_2CO$.

(5) Mechanism IV is the only bimolecular process for which a species appearing in the reaction path lies substantially above the reactants. Thus, though the reaction begins with the formation of a stable adduct, decomposition of this adduct involves a high activation energy, and the corresponding TS is 18.7 kcal/mol above the reactants. Thus, the process appears to be significantly less favorable than the other bimolecular reactions.

(6) Mechanism VI displays an energy profile quite similar to the unimolecular process I. It is not expected to play an important role since secondary ozonide formation should prevail at the first stage of the reaction with formaldehyde.

In principle, the bimolecular processes II, III, and V may compete. One should keep in mind, however, that the concentration of water in the atmosphere is much higher that that of SO_2 or H_2CO. Thus, mechanism II is probably the main path for the formation of carboxylic acids, although reactions of carbonyl oxide with other species (present in lower amounts) are energetically more favorable.

4. Conclusions

Our calculations suggest that the formation of formic acid in the atmosphere can take place through unimolecular or bimolecular processes. The first case should apply for vibrationally excited carbonyl oxide formed in the ozonolysis of olefins, whereas the second may be envisaged after stabilization. Energetically, the reaction with formaldehyde is particularly favorable, even if the isomerization assisted by other species cannot be ruled out. Under atmospheric conditions, however, the reaction with water should play the major role because of the high concentration of H_2O with respect to other potential reactants.

The reaction of carbonyl oxide with formaldehyde follows a mechanism similar to that proposed by Criegge for the ozonolysis in solution, except that the secondary ozonide decomposes through a radical pathway. Along this pathway, there is formation of hydroxymethyl formate (HMF), the decomposition of which yields HCOOH and regenerates H_2CO. The activation energy for the latter process (21.8 kcal/mol) is slightly lower than that (22.7 kcal/mol) involved in the reaction of HMF with singlet O_2, a process that has been invoked to explain formic acid anhydride (FAA) formation.[45]

JA000731Z

---

(68) (a) Atkinson, R.; Lloyd, A. *J. Phys. Chem. Ref. Data* **1984**, *13*, 315. (b) Horie, O.; Moortgat, G. K. *Atmos. Environ.* **1991**, *25A*, 1881.