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Reaction of FO Radicals with CO: An ab Initio Study of the Reaction Mechanism

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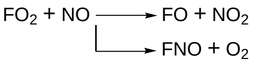
The FO + CO → F + CO_2 reaction is studied by ab initio molecular orbital calculations. The potential energy surface of the reaction system is explored with second-order Møller−Plesset perturbation theory, quadratic configuration interaction (QCISD) method, and Brueckner theory. QCISD(T) methods are used to compute the energetics. The mechanism of the reaction is proposed for the first time. It is found that the FOCO intermediate is transient with respect to dissociation to F and CO_2, and the addition of FO to CO is the rate-determining step. The best estimate for the heat of reaction is −75.8 kcal mol^{-1} at the QCISD(T)/6-311+G(3df)//QCISD/6-31G(d) level of theory. At the same level of theory, the activation barrier height of the overall reaction is estimated to be 10.9 kcal mol^{-1}. These results are consistent with experimental values. The FO + CO reaction is compared with the OH + CO reaction.

I. Introduction

The gas-phase chemistry of halogen monoxide (XO where X = Cl and Br) has long been of atmospheric interest because of its role in catalytic cycles for ozone destruction. The chemistry of inorganic fluorine oxides has not received as much attention as chlorine oxides and bromine oxides. The reason is that the fluorine atom produced almost exclusively from the photooxidation of the CFCs has largely been assumed to be scavenged by water and methane to form stable hydrogen fluoride,[1,2] which is usually rained out of the atmosphere. However, fluorine atoms can also rapidly react with molecular oxygen to produce fluorine peroxide (FO_2) radical.

$$F + O_2 + M \rightarrow FO_2 + M \qquad (1)$$

The equilibrium ratio of FO_2 to F has been estimated as 10^4 in the stratosphere.[3] Fluorine peroxy radicals are oxidized to fluorooxy radicals by reactions with NO viz



$$FO_2 + NO \longrightarrow FO + NO_2; \quad FO_2 + NO \longrightarrow FNO + O_2 \qquad (2)$$

It is important to study the FO reactions not only to compare the results with those for the ClO, BrO, and IO reactions but also to elucidate the possible contribution of FO radicals to the fluorine chemistry in the upper atmosphere. In early works we found that the reaction of FO radicals with water and methane are considerably slow.[4,5] The barrier heights of the two reactions are 25.7 and 16.1 kcal mol^{-1}, respectively. We also explored the possibility of FO radical removal by major atmospheric trace species such as HO and HO_2 radicals.[6,7]

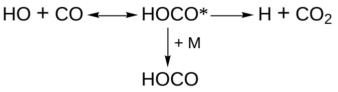
The objective of this work is to examine the mechanism and plausibility of the reaction of fluorooxy radicals with carbon monooxide

$$FO + CO \rightarrow F + CO_2 \qquad (3)$$

The analog reaction of hydroxyl (HO) radicals with CO plays an important role in combustion processes and in atmosphereic chemistry:

$$HO + CO \rightarrow H + CO_2 \qquad (4)$$

This reaction is thought to be the main sink for atmospheric CO.[8] Smith et al. suggested the current accepted mechanism for the overall reaction of HO with CO:[9]



$$HO + CO \longleftrightarrow HOCO^* \longrightarrow H + CO_2; \quad HOCO^* \xrightarrow{+M} HOCO \qquad (5)$$

This reaction has been extensively studied experimentally.[9−12] The *trans*-HOCO intermediate involved in the reaction has been recently characterized experimentally in gas phase.[12] Numerous ab initio studies of reaction 4 were reported.[13a−c]

There are two experimental works about the FO + CO reaction which were reported.[14,15] Bauer et al. showed that the reaction FO + CO did produce CO_2[14] and gave a rate constant 7.5×10^{10} cm^3 mol^{-1} s^{-1} at a temperature range of 900−1400 K. Bedzhanyan et al.[15] reported rate constants for the reaction FO + CO → products as $k < 4 \times 10^{-17}$ and $< 5 \times 10^{-16}$ cm^3 s^{-1} at 300 and 550 K, respectively. In order to explain the experimental results in their study of the thermal reaction between F_2O and CO,[16] Croce and co-workers postulated that reaction 3 produced FOCO as an intermediate in CO_2 formation. However, no studies to date have deduced the mechanism. There is no theoretical work regarding the FO + CO reaction reported in the literature. In the present work, ab initio molecular orbital calculations are carried out to determine the potential energy surfaces of reaction 3. The details of the reaction mechanism are discussed.

II. Computational Methods

Ab initio molecular orbital calculations are performed using the GAUSSIAN 92 program.[17] Using 6-31G(d)[18] and 6-311G(d) basis sets,[19] geometries of all the reactants, products, and transition states are fully optimized at the unrestricted second-order Møller−Plesset perturbation (UMP2) level of theory with all orbitals active. The quadratic configuration interaction theory using single and double excitations method (QCISD/6-31G(d)) is also used to optimize the geometries. Harmonic vibrational frequencies and zero-point energies are computed at the QCISD/6-31(d) level of theory. Quadratic configuration interaction theory using single, double, and triple excitations (QCISD(T))

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TABLE 1: Optimized Geometries of Species Involved in the FO + CO Reaction System[a]

species	coordinate	theory level UMP2/6-31G(d)	theory level UQCISD/6-31G(d)
FO	FO	1.344	1.381
CO	CO	1.150	1.145
CO_2	CO	1.179	1.172
FOCO (*trans*)	CO_1	1.357	1.367
	CO_2	1.194	1.188
	FO	1.452	1.440
	OCO	123.2	123.2
	FOC	105.3	105.4
FC(O)O	CO_1	1.193	1.221
	CO_2	1.329	1.275
	CF	1.339	1.326
	FCO_1	126.5	122.6
	FCO_2	107.9	116.1
$[FO + CO]^{\ddagger}_{cis}$	CO_1	1.834	1.805
	CO_2	1.152	1.151
	FO	1.371	1.419
	OCO	125.7	124.8
	FOC	104.1	103.7
$[FO + CO]^{\ddagger}_{trans}$	CO_1	1.816	1.797
	CO_2	1.153	1.152
	FO	1.363	1.411
	OCO	121.5	120.6
	FOC	106.9	106.1
$[trans-cis]^{\ddagger}$	CO_1	1.435	1.441
	CO_2	1.173	1.180
	FO	1.416	1.444
	OCO	126.9	126.6
	FOC	101.5	101.5
	dih (FOCO)	95.4	92.6
$[trans \rightarrow F + CO_2]^{\ddagger}$	CO_1	1.246	1.302
	CO_2	1.193	1.192
	FO	1.445	1.530
	OCO	145.2	132.9
	FOC	106.7	104.0

[a] Bond lengths in angstroms, angles in degrees.

is used to improve the energetics. The QCISD/6-31G(d) geometries is used to do the energetic calculation. The electronic structures of the FOCO intermediates are also explored by Bruecker theory with triple substitution (BD(T)).[20]

III. Results and Discussion

Table 1 contains optimized geometries for all the species involved in the reaction FO + CO system; the corresponding total energies are given in Table 2, and the vibrational frequencies and zero-point energies are presented in Table 3. Relative energies of the reactions involved are listed in Table 4.

A. Isomers of FOCO. There are two intermediates that could be involved in the FO + CO reaction: (1) an FOCO radical and (2) and FC(O)O radical. We have optimized the structures for both intermediates. For the FOCO radical there are two possible structural forms, a *cis* and a *trans* rotamer, with the FOCO dihedral angle $\tau = 0°$ and $\tau = 180°$, respectively. The MP2 theory failed to determine the structure of the *trans*-FOCO intermediate. With the quadratic configuration interaction theory using the single and double excitations method (QCISD/6-31G(d)), the *trans*-FOCO structure was located and optimized. The internal C−O bond in the *trans*-FOCO structure is 1.367 Å. This bond is intermediate between a single and double C−O bond character. The F−O bond is elongated by 0.059 Å in the *trans*-FOCO radical compared with the F−O bond in the FO radical. Spin densities analysis shows that the unpaired electron in the radical is delocalized across the C−O bonds. The delocalization weakens the F−O bond in the *trans*-FOCO radical. On the other hand, for the

TABLE 2: Total Energy (hartrees) for Species Involved in the FO + CO Reaction System

level of theory	FO	CO	F	CO_2	FOCO (*trans*)	FC(O)O (C_s)	$[FO + CO]^{\ddagger}_{cis}$	$[FO + CO]^{\ddagger}_{trans}$	$[trans \rightarrow cis]^{\ddagger}$	$[trans \rightarrow F + CO_2]^{\ddagger}$
UMP2/6-31G(d)	−174.442 49	−113.028 18	−99.489 04	−188.118 36		−287.611 34	−287.448 80	−287.449 09	−287.464 07	
UQCISD/6-31G(d)	−174.463 41	−113.036 23	−99.499 54	−188.116 52	−287.498 04	−287.634 19	−287.475 89	−287.476 72	−287.480 72	−287.493 42
QCISD(T)/6-311G(d)//UQCISD/6-31G(d)	−174.563 50	−113.093 80	−99.565 80	−188.215 72	−287.656 05	−287.788 11	−287.635 11	−287.636 05	−287.638 42	−287.653 64
QCISD(T)/6-311G(2d)//UQCISD/6-31G(d)	−174.606 56	−113.117 16	−99.586 28	−188.256 13	−287.724 65	−287.854 67	−287.704 73	−287.705 05	−287.707 06	−287.721 67
QCISD(T)/6-311+G(2d)//UQCISD/6-31G(d)	−174.615 54	−113.120 25	−99.592 09	−188.262 92	−287.737 01	−287.866 33	−287.717 40	−287.717 71	−287.719 40	−278.734 86
QCISD(T)/6-311G(2df)//UQCISD/6-31G(d)	−174.651 42	−113.147 83	−99.608 35	−188.315 51	−287.806 00	−287.939 49		−287.782 50		−287.802 85
QCISD(T)/6-311+G(2df)//UQCISD/6-31G(d)	−174.660 10	−113.150 58	−99.613 91	−188.321 41	−287.817 58	−287.949 77		−287.794 49		−287.815 21
QCISD(T)/6-311+G(3df)//UQCISD/6-31G(d)	−174.667 62	−113.157 28	−99.617 80	−188.332 24		−287.966 66		−287.809 39		

TABLE 3: Vibrational Frequencies for Species Involved in the FO + CO Reaction System

	UQCISD/6-31G(d)	
	frequencies (cm^{-1})	ZPE (kcal/mol)
FO	1021	1.5
CO	2176	3.1
CO_2	658, 658, 1368, 2425	7.3
FOCO (*trans*)	260, 374, 583, 1011, 1096, 1900	7.4
FC(O)O (C_s)	467, 554, 752, 985, 1277, 1597	8.1
$[FO + CO]^{\ddagger}_{cis}$	633i, 121, 187, 417, 1056, 2075	5.5
$[FO + CO]^{\ddagger}_{trans}$	586i, 119, 232, 401, 1040, 2072	5.5
$[trans \rightarrow cis]^{\ddagger}$	295i, 324, 581, 836, 1072, 1868	6.7
$[trans \rightarrow F + CO_2]^{\ddagger}$	1246i, 324, 352, 764, 954, 1923	6.1

cis-FOCO, the MP2 theory does locate a local minimum. However, this minimum is not reproduced at higher levels of theory, such as the QCISD(T) and BD(T) using the 6-31G(d) basis set.

To analyze the effect of the level of theory on the shape of the potential surface, a number of calculations were performed along an approximate reaction path obtained from the MP2/6-31G(d) calculations. For the *cis*-FOCO, 11 points along the MP2/6-31G(d) reaction path were chosen: three interpolated points and seven extrapolated points beyond the local minimum. The energy profiles calculated with the 6-31G(d) basis set using a variety of electron correlation methods are depicted in Figure 1. The UMP2 profile exhibits a local minimum and a curve crossing later along the reaction path as shown in Figure 1a. But we show in Figure 1b,c that this minimum is not reproduced at the higher levels of theory. We have also performed ROMP2/6-31G(d) calculations and find that there is no local minimum on this surface (see Figure 1d). Consequently, the minimum found for the *cis*-FOCO structure at the UMP2 level is an artifact of the Møller−Plesset perturbation theory. From these results, we conclude that the *cis*-FOCO does not exist. The singly occupied orbital on the carbon atom readily interacts with the FO σ^* orbital, leading to the facile dissociation of the F−O bond.

For the *trans*-FOCO, nine points along the MP2/6-31G(d) reaction path were chosen, as shown in Figure 2a. The energy profiles calculated at higher levels of theory with the 6-31G(d) basis set are shown in Figure 2b,c. Once again, perturbation theory does not treat the electronic structure of this system properly. As a result, the UMP2 potential surface does not have a stationary point. At the ROMP2/6-31G(d) level, we did find a minimum on this surface (see Figure 2d). We also performed higher levels of calculation that include single excitations in an iterative, rather than perturbative treatment, in order to treat the avoided crossing properly. At the higher level we obtained a stationary point that corresponds to the *trans*-FOCO intermediate. As shown above, the FOCO intermediate is one of a small number of cases where the UMP2 theory is qualitatively incorrect.

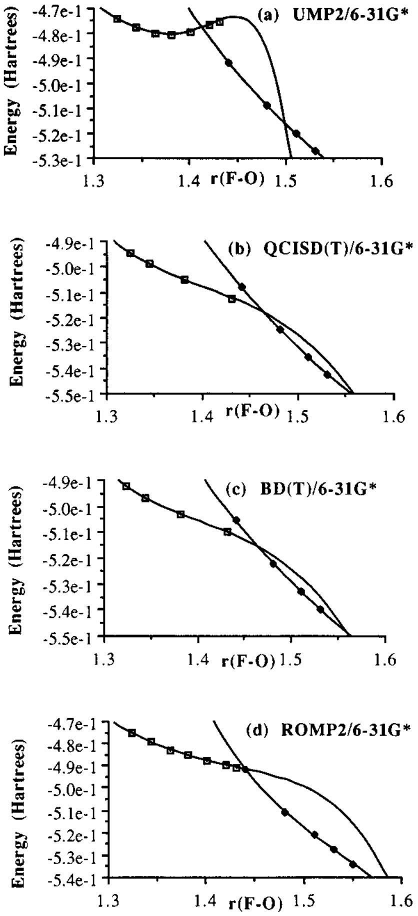

Figure 1. Potential energy curves for *cis*-FOCO intermediate at various levels of theory along the F−O bond pathway. The energy is the total energy at each point plus 287.0 hartree. (a) At the UMP2/6-31G* level of theory. (b) At the QCISD(T)/6-31G* level of theory. (c) At the BD(T)/6-31G* level of theory. (d) At the ROMP2/6-31G* level of theory.

We have been able to locate the rotational transition state from the *trans*-FOCO structure going to the *cis*-FOCO structure, as shown in Figure 3a. The FOCO dihedral angle in the transition state is $\tau = 92.6°$. The rotational transition state reflects the rotation about the FO−CO bond: the fluorine rotates from the *trans* position ($\tau = 180°$) into the *cis* position ($\tau = 0°$). The rotational transition state is a first-order saddle point with one imaginary frequency of 295i. The rotational barrier is 10.9 kcal mol^{-1} relative to the *trans*-FOCO at the QCISD(T)/6-311+G(3df)//QCISD/6-31G(d) level of theory.

An isomer of the FOCO radical is the FC(O)O radical. This radical was first postulated by Francisco and Ostafin to have C_{2v} and C_s structures,[21] with the C_{2v} being the lower energy structure. The existence of this radical was experimentally verified by Maricq et al.[22] Structural results presented in the present work are consistent with those from earlier studies of Francisco and Ostafin.[21]

We have done preliminary searches for the isomerization pathway between FOCO and FC(O)O radicals. We located a

TABLE 4: Activation Barrier Heights (kcal mol^{-1}) for the FO + CO Reaction System

level of theory	$[FO + CO]^{\ddagger}_{trans}$	$[FO + CO]^{\ddagger}_{cis}$	$[trans \rightarrow cis]^{\ddagger}$	$[trans \rightarrow F + CO_2]^{\ddagger}$
UMP2/6-31G(d)	13.5	13.7		
UQCISD/6-31G(d)	14.4	14.9	10.9	2.9
UQCISD(T)/6-311G(d)//UQCISD/6-31G(d)	13.3	13.9	11.1	1.5
UQCISD(T)/6-311G(2d)//UQCISD/6-31G(d)	11.7	11.9	11.0	1.9
UQCISD(T)/6-311+G(2d)//UQCISD/6-31G(d)	11.3	11.5	11.1	1.3
UQCISD(T)/6-311G(2df)//UQCISD/6-31G(d)	10.5	10.8	11.5	2.0
UQCISD(T)/6-311+G(2df)//UQCISD/6-31G(d)	10.2			1.5
UQCISD(T)/6-311+G(3df)//UQCISD/6-31G(d)	9.7	10.0	11.6	1.6
UQCISD(T)/6-311+G(3df)//UQCISD/6-31G(d)+ΔZPE	10.6	10.9	10.9	0.3

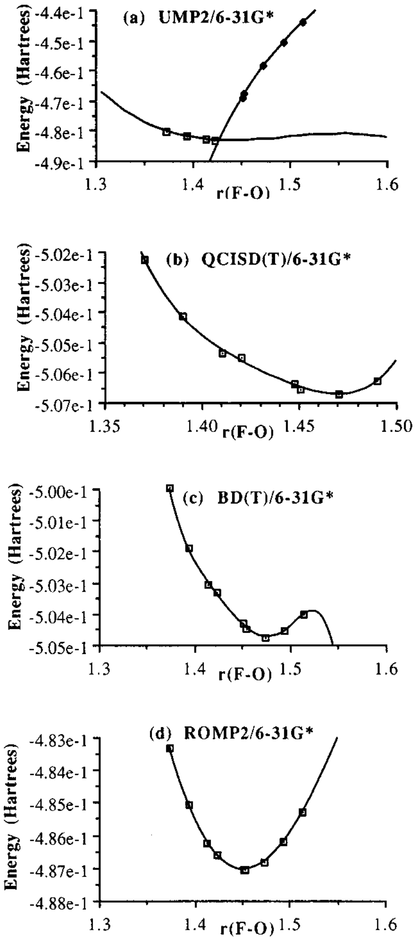

Figure 2. Potential energy curves for *trans*-FOCO intermediate at various levels of theory along the F−O bond pathway. The energy is the total energy at each point plus 287.0 hartree. (a) At the UMP2/6-31G* level of theory. (b) At the QCISD(T)/6-31G* level of theory. (c) At the BD(T)/6-31G* level of theory. (d) At the ROMP2/6-31G* level of theory.

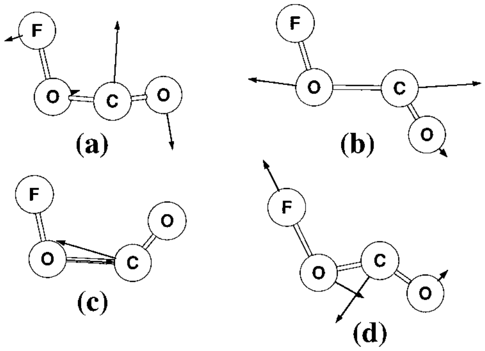

Figure 3. Transition states of the FO + CO reaction system calculated at the QCISD/6-31G(d) level of theory. (a) $[trans-cis]^{\ddagger}$ (b) $[\mathrm{FO}+\mathrm{CO}]^{\ddagger}_{\mathrm{trans}}$ (c) $[\mathrm{FO}+\mathrm{CO}]^{\ddagger}_{\mathrm{cis}}$ (d) $[trans \rightarrow \mathrm{F}+\mathrm{CO}_2]^{\ddagger}$

saddle point that is 58.2 kcal mol^{-1} above the *trans*-FOCO structure at the QCISD(T)/6-311G(2d) level of theory. Consequently, FOCO radicals are unlikely to isomerize to form FC(O)O radicals.

B. Addition of FO to CO. The reaction of FO radicals with CO can take place from two directions: *trans* addition of FO to CO to produce *trans*-FOCO intermediate and the *cis* addition of FO to CO. We have located the two transition states at the MP2 and QCISD levels of theory. As shown in Figure 3b, at QCISD/6-31G(d) level of theory, the forming CO$_1$ bond for the *trans* addition is 1.797 Å, which is much longer than the 1.367 Å in the *trans*-FOCO intermediate. Also, the F−O bond in the transition state is 0.029 Å shorter than that in the *trans*-FOCO. This suggests that the delocalization of the unpaired electron takes place later along the reaction coordinate. In the transition state for the *cis* addition of the FO radicals to CO, the forming CO$_1$ bond and the F−O bond are 1.805 and 1.419 Å, respectively, as shown in Figure 3c. This transition state is also more reactant-like.

The barrier for the *trans* addition of FO + CO is 10.6 kcal mol^{-1} at the QCISD(T)/6-311+G(3df)//QCISD/6-31G(d) level of theory, and for the *cis* addition of FO to CO, the barrier is 10.9 kcal mol^{-1} at the same level (including ZPE correction). Both transition structures are true first-order saddle points, with imaginary frequencies 586i and 633i for *trans* and *cis* addition transition states, respectively. It is interesting to note that both the *cis* and the *trans* addition barriers are higher than the *cis*−*trans* rotational barrier: 2.1 kcal mol^{-1} higher for the *trans* route and 2.4 kcal mol^{-1} higher for the *cis* route.

C. Dissociation of FOCO Intermediates. Since the barrier for isomerization from the *trans*-FOCO intermediate to FC(O)O is significantly high and the rotational barrier from the *trans*- to the *cis*-FOCO is lower than both of the FO + CO additional barriers, isomerization does not play a major role in establishing the lifetime of FOCO radicals. The critical factor that determines the chemical lifetime of the FOCO radical is the barrier for dissociation of FOCO to F and CO$_2$. At the QCISD/6-31G(d) level of theory, the activation barrier for the *trans*-FOCO dissociation to F and CO$_2$ is 2.9 kcal mol^{-1}. The transition state is shown in Figure 3d. The dissociation barrier is lowered to 1.6 kcal mol^{-1} by using the QCISD(T) method with the largest basis set, 6-311+G(3df). We did a single-point calculation for the barrier with the fourth-order Møller−Plesset perturbation theory in the space of single, double, triple, and quadruple excitations (PMP4) and found the barrier to be nearly 4 kcal mol^{-1} higher than the QCISD result. This is another indication that the unrestricted perturbation theory does not treat the interaction properly in the case of FOCO intermediate.

We know that the *cis* addition of FO to CO will immediately follow a pathway toward dissociation into F atom and CO$_2$. While for the *trans*-FOCO case at the QCISD(T)/6-311+G(2df)//QCISD/6-31G(d) level of theory, the dissociation barrier to F and CO$_2$ is only 0.3 kcal mol^{-1} with ZPE correction. Compared with the 13.0 kcal mol^{-1} barrier for *trans*-FOCO dissociation back to FO and CO, it is obvious that the *trans*-FOCO intermediate is also transient with respect to dissociation to F and CO$_2$.

In their earlier work, Francisco et al. found that the FC(O)O radical, one of the isomers of FOCO, will dissociate to F and CO$_2$ with a 24.3 kcal mol^{-1} barrier at the UMP2/6-31G(d) level of theory.[23]

D. Summary of the FO + CO → F + CO$_2$ Reaction. The present calculations suggest the following about the mechanism for the FO + CO reaction: (1) The first step of the reaction is the addition of FO radicals to CO. The *trans* addition produces the *trans*-FOCO intermediate, and the *cis* addition leads to F and CO$_2$ directly. The activation barrier for the two addition pathways are 10.6 and 10.9 kcal mol^{-1}, respectively, at the QCISD(T)/6-311+G(3df) level of theory. Since the two barriers are nearly equal, the two pathways may occur in parallel. (2) From the *trans* approach, the next step is the dissociation of the FOCO intermediate to F and CO$_2$. The dissociation of the *trans*-FOCO structure to F and CO$_2$ is very exothermic, and there is a very low activation barrier (0.3 kcal mol^{-1}). Consequently, once the *trans* addition barrier is surmounted, it is likely that the *trans*-FOCO intermediate dissociates to F and CO$_2$. (3) The rotation from the *trans*- to the *cis*-FOCO

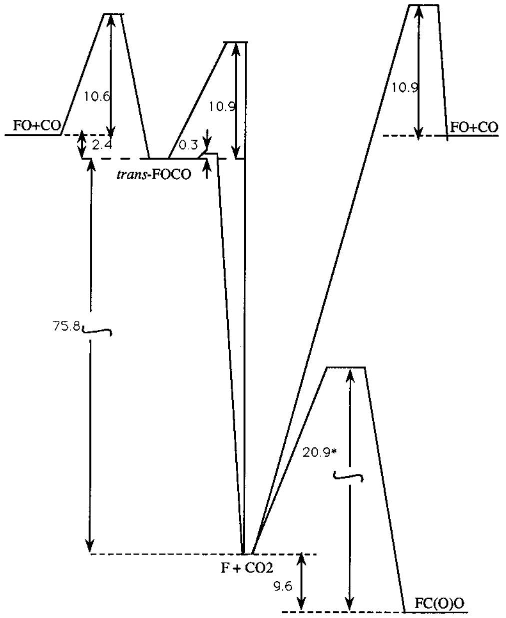

Figure 4. Schematic diagram of the potential energy surface for the FO + CO reaction system calculated at the QCISD(T)/6-311+G(3df) level of theory with QCISD/6-31G(d) geometry (in kcal mol^{-1}).

intermediate is not important. The isomerization of the *trans*-FOCO intermediate to FC(O)O should not occur because of a very high activation barrier.

From our survey of the mechanism of the FO + CO reaction, we find that the only major products of the reaction are F and CO_2. The pathways by which these are produced are shown in Figure 4. There are two experimental studies of the FO + CO reaction.[14,15] Bauer et al. showed that the reaction produced CO_2.[14] The observation of this product is consistent with the mechanism proposed here. From the rates reported by Bauer over the temperature range of 900−1400 K, an activation barrier of about 11 kcal mol^{-1} was suggested. From the rates reported by Bedzhanyan at 300 and 550 K,[15] we can extrapolate a barrier of 3.3 kcal mol^{-1}. The two experimental results appear inconsistent. However, the calculated barrier for the rate-limiting step, the FO + CO addition, is 10.9 kcal mol^{-1}. Our calculated barrier is consistent with the results of Bauer.[14]

A comment regarding the mechanism proposed by Croce et al.[16] is pertinent at this point. In order to explain the experimental results, Croce and co-workers postulated the FOCO radical as a reaction intermediate, followed by two reactions involving FOCO:

$$\mathrm{FO + CO \rightarrow FOCO} \tag{6}$$

$$\mathrm{FOCO + CO \rightarrow FCO + CO_2} \tag{7}$$

$$\mathrm{FOCO + FCO \rightarrow CF_2O + CO_2} \tag{8}$$

They also assumed that the activation energy for reaction 7 is about 8 kcal mol^{-1}. From our calculations, we conclude that the FOCO intermediate should be transient; it will lead to the F atom and CO_2. It is unlikely that FOCO radicals can be involved in a reaction collision process with CO or FCO radicals. So we suggest that reactions 6−8 be replaced by reaction 3 and the following two elementary reactions:

$$\mathrm{F + CO \rightarrow FCO} \tag{7$'$}$$

$$\mathrm{F + FCO \rightarrow CF_2O} \tag{8$'$}$$

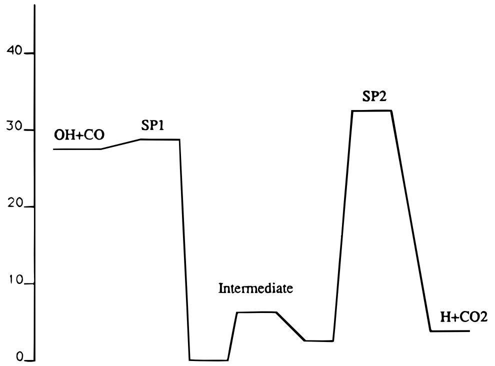

Figure 5. Schematic diagram of the HO + CO potential surface based on the ab initio calculation by Aoyagi and Kato (ref 13c) (in kcal mol^{-1}).

These reactions can also account for the observed products. The rate constant of reaction 7′ has been measured by Wallington and co-workers[24] and Baulch et al.[25]

E. Comparison of the FO + CO Reaction with the HO + CO Reaction. It is interesting to compare the FO + CO reaction with the HO + CO reaction. A schematic diagram of the HO + CO → H + CO_2 potential surface based on the ab initio calculations of Shatz et al. and Aoyagi and Kato[13b,c] is shown in Figure 5. For the HO + CO reaction, the first step is the *trans* addition of HO to CO, followed by *trans*−*cis* isomerization leading to the elimination of hydrogen from the *cis*-HOCO intermediate. It is also found that the tunneling effect of the H atom from HOCO is important to reproduce the observed reaction rates.

Comparing the FO + CO reaction with the HO + CO reaction, we can see the following differences: (1) The barrier for *trans* addition was calculated to be 6.4 kcal mol^{-1} lower than that of *cis* addition of HO to CO; consequently, the *trans* HO + CO addition is favored. Only the *trans*-HOCO is observed experimentally. However, for the FO + CO addition, since the *trans* and *cis* addition barriers are nearly equal, either approach should produce the products F atom and CO_2. (2) The barrier for dissociation of FOCO to F and CO_2 is very low, while for hydrogen elimination of HOCO, the barrier height for *cis* elimination was calculated to be 35.3 kcal mol^{-1}, and it is found that the hydrogen tunneling is dominant. (3) The isomerization of the FOCO intermediate is not important, while for HO + CO, the *trans*−*cis* isomerization is essential because the energy of *cis* elimination is lower than the *trans* elimination by 19.6 kcal mol^{-1}. Finally, the activation barrier for the addition of FO to CO is much higher than that for the addition of HO to CO (10.9 vs 2.9 kcal mol^{-1}).

IV. Conclusion

The potential energy surface of the FO + CO → F + CO_2 reaction has been examined by using Møller−Plesset perturbation theory and quadratic configuration interaction methods. The FOCO intermediate is found as one of a small number of cases where unrestricted MP2 theory gives qualitatively and quantitatively incorrect results. All the transition states involved in the reaction system have been located and optimized. The complete reaction mechanism was suggested for the first time based on ab initio calculations. The heat of reaction is estimated as −75.8 kcal mol^{-1} at the QCISD(T)/6-311+G(3df) level of theory, which agreed with the experimental estimation of −76.1 kcal mol^{-1} (estimated from the heats of formation of FO, CO, F, and CO_2). Our best estimate of the activation energy for the overall reaction is 10.9 kcal mol^{-1} at the same level of theory. This value is in agreement with the experimental estimate of the activation energy, 11 kcal mol^{-1}, suggested by Bauer et al.[14]

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