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Ab Initio Study of the Oxidation Reaction of CO by ClO Radicals

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The oxidation of carbon monoxide by ClO radicals was studied by ab initio molecular orbital theory calculations. Geometry optimizations and vibrational frequencies were computed using two methods: Møller−Plesset second-order perturbation theory (MP2), and quadratic configuration interaction in the space of single and double excitations (QCISD). Single-point energy calculations were performed at the QCISD level with triple excitations treated perturbatively (QCISD(T)) and the aug-cc-pVTZ basis set. Canonical transition state theory was used to predict the rate constants as a function of temperature (550−2500 K), and three-parameter Arrhenius expressions were obtained by fitting to the computed rate constants. The possible impact of the title reaction in combustion chemistry is also discussed.

Introduction

To model the high-temperature oxidation processes occurring in the incineration of chlorinated hazardous wastes, kinetic data concerning the reactivity of chlorooxy radicals with major species such as carbon monoxide are needed. A recent study[1] of the ignition and combustion of ammonium perchlorate in a hydrogen atmosphere showed that ClO radicals are generated at 1400 K near the surface of the burner at the same level of concentration as the OH radicals. To the best of our knowledge, this is the first time that ClO radicals have been detected in flames including chlorinated compounds. Studies[2] of the equilibrium product distributions associated with the combustion of CH_3Cl, CH_2Cl_2, and $CHCl_3$ in air show that the mole fractions of ClO radicals under fuel lean conditions (equivalence ratio $\varphi = 0.5$) are at least 100 as high as the ones of OH radicals at temperatures lower than 900 K and remain predominant until about 1100, 1500, and 1800 K for CH_3Cl, CH_2Cl_2, and $CHCl_3$, respectively. These estimates suggest that ClO might contribute to the oxidation of CO to CO_2 in the combustion of chlorinated hydrocarbons under air excess conditions. This contribution is expected to be largely predominant in oxidation processes of chlorinated organic species without hydrogen atoms. Very few determinations of the rate constant of the reaction ClO + CO → Cl + CO_2 have been published in the literature. Clyne and Watson[3] reported an upper limit to the rate constant at 587 K ($k < 2.0 \times 10^{-15}$ cm^3·molecule^{-1}·s^{-1}) for the reaction between ClO and CO. On the basis of these data, DeMore et al.[4] have estimated the following rate expression over the atmospheric temperature range (200−300 K):

$$k = 1.0 \times 10^{-12}\ (\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}) \times \exp(-30764\ (\text{J}\cdot\text{mol}^{-1})/RT) \quad (1)$$

where the activation energy is assumed to be a lower limit.

To assess the relevance of the title reaction in the incineration of chlorinated hazardous waste, it is important to understand the mechanisms and kinetics of this reaction at combustion temperatures. High-level ab initio molecular orbital theory can be very helpful in the prediction of the kinetic parameters over a wide temperature range and in the understanding of the details of the mechanism governing the reaction ClO + CO → Cl + CO_2. In this work, we apply this methodology combined with canonical transition state theory, to study the temperature dependence of the kinetics of this reaction. To our knowledge, this is the first theoretical study of the reaction between ClO and CO.

Computational Methods[5]

All calculations described were carried out with the Gaussian 98[6] suite of programs on a 4-processor Compaq, 32-processor NEC SX-5, and 32-processor Silicon Graphics Origin 2000 parallel computers. Fully optimized geometries, harmonic vibrational frequencies, and zero-point energy corrections (ZPE) of reactants, transition states, molecular complexes and products, were calculated with the unrestricted second-order Møller−Plesset perturbation theory (UMP2)[7] using the 6-311G(d) basis set.[8] Electron correlation was computed with second-order Møller−Plesset perturbation theory with full annihilation of spin contamination[9] as implemented in the Gaussian 98 package (noted PMP2 in our results). To confirm the connection of the transition states with reactants and products, the reaction path was followed using IRC[10] (intrinsic reaction coordinate) calculations at the UMP2/6-311G(d) level. The geometrical parameters were reoptimized with the unrestricted quadratic configuration interaction theory using single and double excitations method[11] (UQCISD) and the 6-311G(d) basis set. Harmonic vibrational frequencies were also computed numerically at the UQCISD/6-311G(d) level. The geometries previously optimized at the QCISD/6-311G(d) level were used in order to perform single-point energy calculations for all species at the quadratic configuration interaction level of theory using single, double, and triple excitations, QCISD(T),[11] and basis sets ranging from

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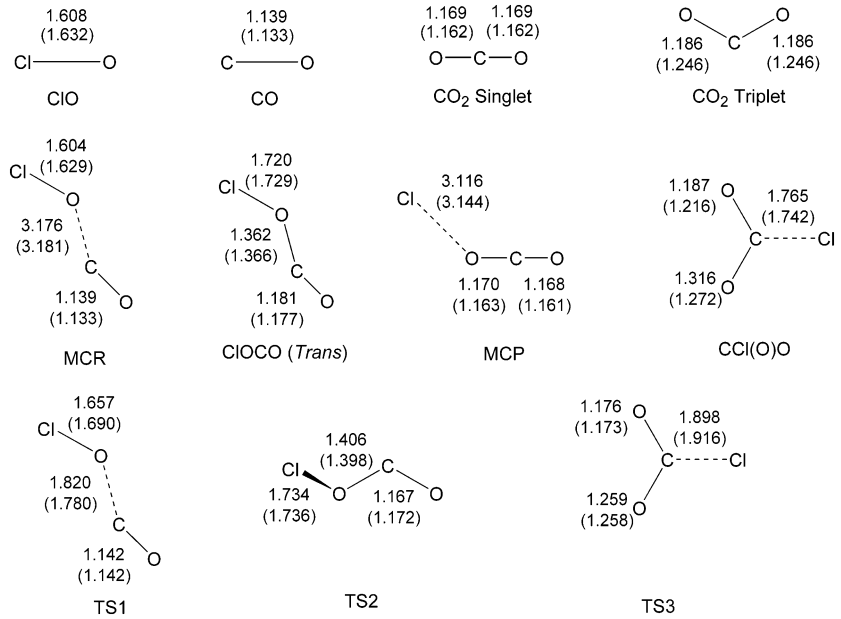

Figure 1. Structures optimized at UMP2/6-311G(d) and QCISD/6-311G(d) levels of theory for the reactants, products, and intermediate species. Bond lengths are in ångstroms. The values in parentheses correspond to the QCISD/6-311G(d) calculations.

TABLE 1: Optimized Geometry Parameters[a] for Intermediate Species Calculated at UMP2/6-311G(d) and UQCISD/6-311G(d) Levels of Theory

parameter	MCR	TS1	ClOCO (trans)	TS2	MCP	TS3	CCl(O)O
$r(C-O_1)$	1.139 (1.133)	1.142 (1.142)	1.181 (1.177)	1.167 (1.172)	1.168 (1.161)	1.176 (1.173)	1.187 (1.216)
$r(C-O_2)$	3.176 (3.181)	1.820 (1.780)	1.362 (1.366)	1.406 (1.398)	1.170 (1.163)	1.259 (1.258)	1.316 (1.272)
$r(Cl-O_2)$	1.604 (1.629)	1.657 (1.690)	1.720 (1.729)	1.734 (1.736)	3.116 (3.144)		
$r(C-Cl)$						1.898 (1.917)	1.765 (1.742)
$\theta(O_2CO_1)$	102.0 (104.9)	120.9 (120.0)	124.2 (124.2)	128.8 (128.4)	179.9 (179.9)	143.1 (142.9)	128.1 (121.5)
$\theta(ClO_2C)$	94.7 (94.9)	114.9 (113.9)	112.0 (112.0)	109.2 (110.1)	136.8 (136.9)		
$\theta(ClCO_1)$						124.3 (122.8)	126.6 (123.0)
$\phi(ClO_2CO_1)$	188.9 (182.8)	180.0 (180.0)	180.0 (180.0)	94.8 (97.4)	180.3 (179.9)		
$\phi(ClCO_1O_2)$						180.0 (180.0)	180.0 (180.0)

[a] Bond lengths in ångstroms, angles in degrees; values in parentheses correspond to the optimized geometries at the UQCISD/6-311G(d) level.

TABLE 2: Vibrational Frequencies and Zero-Point Energy (ZPE) Corrections for Intermediate Species Calculated at UMP2/6-311G(d) and UQCISD/6-311G(d) Levels of Theory

species	vibrational frequencies (cm^{-1})[a]	ZPE ($kJ \cdot mol^{-1}$)
MCR	9, 48, 53, 102, 828, 2137	19.0
	8, 50, 53, 105, 776, 2190	19.0
TS1	**671i**, 95, 202, 328, 865, 2095	21.4
	604i, 107, 209, 357, 727, 2082	20.8
ClOCO (trans)	219, 286, 530, 893, 1055, 1886	29.1
	206, 282, 498, 792, 1033, 1897	28.2
TS2	**295i**, 234, 584, 704, 885, 2127	27.1
	291i, 245, 573, 699, 876, 1893	25.6
MCP	14, 59, 656, 657, 1342, 2456	31.0
	12, 56, 673, 674, 1375, 2431	31.3
TS3	**727i**, 415, 429, 660, 1058, 2027	27.4
	555i, 383, 444, 661, 1104, 2014	27.5
CCl(O)O	321, 462, 670, 674, 1127, 1878	30.7
	330, 458, 665, 697, 1168, 1478	28.7

[a] First row represents UMP2/6-311G(d) calculations, and second row, UQCISD/6-311G(d) calculations.

6-311G(d) to the augmented correlation-consistent polarized valence triple-ζ sets,[12] aug-cc-pVTZ, developed by Kendall et al.

Results and Discussion

The structures of all stationary points involved in this reaction are shown in Figure 1. Tables 1 and 2 list the corresponding optimized geometrical parameters, vibrational frequencies, and unscaled zero-point energy corrections (ZPEs). Given that instabilities of the HF/3-21G wave function for the C_{2v} structure of the $ClCO_2$ radical previously observed by Marshall[13] cast some doubts on the applicability of the single-reference treatments of potential energy surfaces involving chlorine and carbon monoxide, stability tests were conducted on the Hartree−Fock (HF) wave functions corresponding to all stationary points optimized in this study. The results show that for all the basis sets used in this work, these stationary points are characterized by stable HF wave functions, providing grounds for confidence on the validity of the single-reference based calculations performed in the present study.

1. Reaction Mechanism and Energetics. *1.1. ClOC•O and CCl(O)O• Radicals.* Given that a concerted addition mechanism could lead to the formation of the ClOC•O and the CCl(O)O• radicals, we decided to characterize the geometrical properties as well as the energetics of these species. The ClOC•O radical can in principle be found in a trans and a cis conformer with the Cl−O−C−O dihedral angle ϕ equal to 180° and 0°, respectively. The trans structure was optimized at both levels of theory (see Figure 1). Direct geometry optimizations at the MP2 and QCISD calculations predict a very unstable cis conformer that decomposes into the more stable system Cl + CO_2 as a result of the cleavage of the Cl−O bond. Similar results were obtained at the UHF[14] and B3LYP[15] levels. To further investigate these results, the rotational potential energy surface (RPES) for the ClOC•O radical was computed at the UMP2/

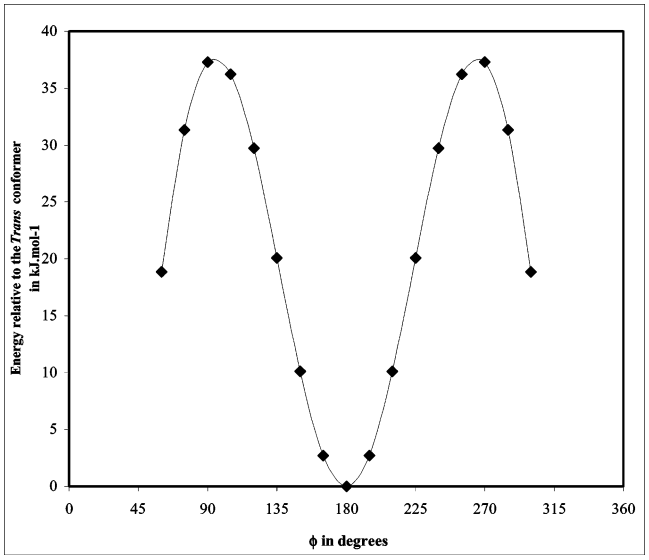

Figure 2. Rotational potential energy surface for the ClOC•O radical calculated at the UMP2/6-311G(d) level of theory.

TABLE 3: Energies of All Stationary Points Relative to ClO + CO Calculated at the QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) Level of Theory Including the ΔZPEs

species	energy/ClO + CO in kJ·mol^{-1}
MCR	−3.0
TS1	48.9
ClOCO (trans)	1.1
TS2	29.9
MCP	−271.2
Cl + CO_2 (singlet)	−266.9
Cl + CO_2 (triplet)	163.9
TS3	−162.1
CCl(O)O	−160.9

6-311G(d) (see Figure 2). The RPES was obtained by performing a relaxed scan starting from the trans conformer ($\phi = 180°$) where ϕ was varied by 15° intervals. As observed in Figure 2, the RPES is characterized by a rotational transition state that connects the trans conformer with a nonstationary point in the vicinity of 60°. The dihedral angle for the corresponding transition structure was found to be equal to 94.8° at the UMP2/6-311G(d) level of theory. This structure is indeed a first-order saddle point with an imaginary frequency of 295i cm^{-1}. In addition, it was found that for ϕ values lower than 60°, the relaxed scan failed to locate a stationary point, suggesting the nonexistence of the cis conformer. Furthermore, IRC calculations indicate that the rotational transition state connects the trans conformer with a Cl···CO_2 molecular complex instead the cis conformer. From these results, we conclude that the *cis*-ClOC•O radical does not exist.

Despite exhaustive searches involving relaxed scans and IRC calculations, we were not able to locate a pathway connecting the ClOC•O and CCl(O)O• radicals, indicating that the isomerization reaction involving these radicals is unlikely. This is in agreement with the QCISD(T)/6-311G(2d) calculations of Su and Francisco[16] on the FO + CO reaction, where a fairly large intrinsic barrier (243.5 kJ.mol^{-1}) for the isomerization *trans*-FOC•O → CF(O)O•, was found.

1.2. ClO + CO Reaction Pathway and Energetics. Table 3 lists the relative energies (computed at QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) level) of the different stationary points located along the ClO + CO reaction pathway, and Figure 3 depicts the corresponding energy profile. The first step of the addition of ClO radicals to carbon monoxide involves the formation of a molecular complex (MCR in Figure 3), which lies approximately 3.0 kJ mol^{-1} below reactants. This complex is characterized by an intermoiety distance of 3.2 Å and is the result of long-range interactions between CO and the ClO radical. MCR undergoes a structural rearrangement that leads to the formation of the *trans*-ClOC•O radical, which lies approximately 1.1 kJ mol^{-1} above reactants. These two stationary points are connected by a transition structure (TS1 in Figure 3), characterized by an OC···OCl bond length of about 1.820 Å, which is significantly larger than the corresponding bond length in the *trans*-ClOC•O intermediate (1.362 Å). The intrinsic barrier for the MCR → *trans*-ClOC•O step was computed to be 52 kJ mol^{-1}. The results of our calculations indicate that once formed, the *trans*-ClOC•O radical undergoes a rotation around the OCl−OC bond that leads to a transition structure (TS2 in Figure 3) 29.9 kJ mol^{-1} higher than reactants with a dihedral angle $\phi = 94.8°$. This transition structure leads to the formation of a molecular complex (MCP in Figure 3), which is approximately 271.2 kJ mol^{-1} more stable than reactants, and that decomposes to the products Cl + $^1CO_2$. As Figure 2 shows, this stationary point is mainly a Cl···CO_2 long-range complex, with a Cl···O bond distance equal to 3.1 Å (computed at the QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) level). In addition, a transition state structure (TS3 in Figure 3), connecting the radical CCl(O)O• and the more stable products Cl + $^1CO_2$ was located at all levels of theory used in this work. After zero point energy corrections are taken into account, it is found that the TS3 energy lies below the energy of CCl(O)O•, indicating that this radical readily dissociates into Cl and $^1CO_2$. Finally, the dissociation of the *trans*-ClOC•O radical to Cl and $^3CO_2$ was found to be significantly endothermic, casting some doubts over the relevance of this step in the studied temperature range.

The theoretical predicted value for the reaction enthalpy at 298 K for the oxidation reaction computed at the QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) level of theory is −268.9 kJ mol^{-1}, which is in good agreement with the corresponding literature value of -263.3 ± 0.4 kJ mol^{-1} on the basis of $\Delta_f H°$ at 298 K for ClO,[17] CO,[18] Cl,[17] and CO_2.[17] This agreement justifies the use of the levels of theory employed in this work.

2. Rate Constant Calculations. Given the mechanism and energetics predicted by our calculations, it would seem reasonable to assume that the bottleneck of the reaction is determined by the entrance channel where the reactive system has to overcome a barrier of approximately 49 kJ mol^{-1} corresponding to the transition structure TS1. Canonical transition state theory[19] (TST) including a semiclassical one-dimensional multiplicative tunneling correction factor was used to predict the temperature dependence of the rate constant. The rate constants, $k(T)$, were computed using the following expression:

$$k(T) = \Gamma(T)\frac{k_B T}{h}\frac{Q_{TS1}(T)}{Q_{ClO}(T)\,Q_{CO}(T)}\exp\left(-\frac{E_0}{k_B T}\right) \qquad (2)$$

where $\Gamma(T)$ indicates the transmission coefficient used for the tunneling correction at temperature T, $Q_{TS1}(T)$, $Q_{ClO}(T)$, and $Q_{CO}(T)$ are the total partition functions for the transition state TS1, ClO radical, and CO at temperature T, E_0 is the vibrationally adiabatic barrier height computed as the difference in energies between the transition state TS1 and reactants, including zero point energy corrections, k_B is Boltzmann's constant, and h is Planck's constant.

The multiplicity of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states and the corresponding energy gap of 320.3 cm^{-1} for ClO between the low-lying electronic states[18] have been explicitly included in

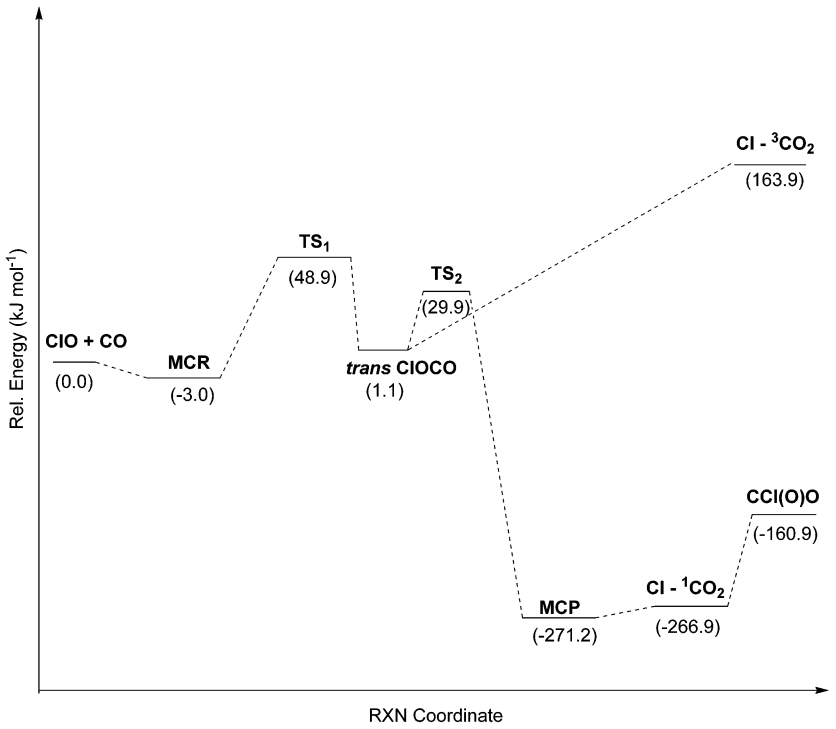

Figure 3. Schematic diagram of the potential energy surface profile for the ClO + CO reaction calculated at the QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) level of theory.

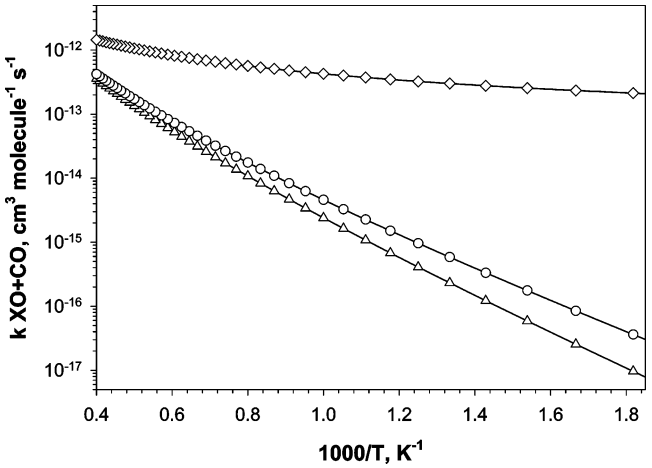

Figure 4. Temperature dependence of the rate constants for HO + CO (diamonds), FO + CO (circles), and ClO + CO (triangles).

the computation of the electronic partition function. All vibrations were treated as harmonic oscillators. We adopt the simple and computationally inexpensive Wigner method[20] in the estimation of the tunneling corrections for the reaction reported in this work:

$$\Gamma(T) = 1 + \frac{1}{24}\left(\frac{h\nu^{\ddagger}}{k_B T}\right)^2 \qquad (3)$$

where $\nu^{\ddagger}$ is the imaginary frequency at the saddle point. This choice seems to be appropriate for the treatment of tunneling corrections of rate constants calculated at typical incineration/combustion temperatures (550−2500 K) for which the values of transmission coefficient $\Gamma(T)$ are close to 1 (e.g., Γ(550 K) = 1.10). Rate constant calculations were carried out over the temperature range of interest using the Turbo-Opt program.[21]

Figure 4 depicts the computed Arrhenius plot in the temperature range 550−2500 K. The rate constants plotted in Figure 4 have been fitted to a three-parameter formula by least-squares, giving the following relation (in units of cm^3·molecule^{-1}·s^{-1}):

$$k(550-2500\ \mathrm{K}) = (4.0 \times 10^{-19}) T^{2.02} e^{(-5265/T)} \qquad (4)$$

It is interesting to note that using eq 4, a value k(587 K) calculated for the rate constant of the ClO + CO reaction is 2 orders of magnitude below the upper limit value proposed by Clyne and Watson[3] (2.0×10^{-17} cm^3 molecule^{-1} s^{-1} vs 2.0×10^{-15} cm^3 molecule^{-1} s^{-1}).

Comparison of the OX + CO → X + CO_2 Reactions (X = Cl or F) to OH + CO → H + CO_2

The reaction OH + CO → CO_2 + H has been extensively studied experimentally and theoretically. The Arrhenius plot for this reaction is depicted in Figure 4. This plot is based on the parameters proposed by Baulch et al.[22] in their 1992 evaluation:

$$k(T) = 5.4 \times 10^{-14}\ (\mathrm{cm^3 \cdot molecule^{-1} \cdot s^{-1}})\ (T/298\ \mathrm{K})^{1.50} e^{(250/T)} \qquad (5)$$

The reaction of FO radicals with CO has been studied theoretically by Su and Francisco.[16] Similar to our results, they found that the addition of FO to CO is the rate-determining step in the complex mechanism. Because no rate constants were computed in their study, we re-optimized the geometries for reactants and the transition structure reported by these researchers using our methodology. Single-point energy calculations were performed at the QCISD(T)/aug-cc-pVTZ//QCISD/6-311G(d) level. Rate constants were calculated over the same temperature range as for the ClO + CO reaction and have been fitted to a three-parameter formula by the least-squares, giving the following relation (in units of cm^3·molecule^{-1}·s^{-1}):

$$k(550-2500\ \mathrm{K}) = (3.2 \times 10^{-19}) T^{2.03} e^{(-4440/T)} \qquad (6)$$

It is observed that over the same temperature range, the rate constants for the reaction FO + CO are close to the corresponding values for the reaction ClO + CO and substantially lower than the ones corresponding to the reaction OH + CO. The lack of experimental data on the ClO concentration profiles under incineration conditions does not enable us to directly compare the rate of ClO + CO reaction with the ones of OH + CO reaction, which is well-known to play an important role in the oxidation of CO. However, ClO and OH concentrations can be reasonably estimated from simulations of a detailed chemical mechanism, leading to a good agreement between the calculated and measured concentration profiles of molecular products generated by the oxidation processes. Numerical simulation of oxidation processes of some chlorinated hydrocarbons can help to better understand the relative importance of these two processes of oxidation of CO to CO_2. In our laboratory,[23] the processes of the thermal oxidation of 1300 ppm (v/v) of CH_2Cl_2 in air were experimentally investigated at 1 atm over the temperature range 973−1173 K and residence times ranging from 0.5 to 3 s. A detailed chemical mechanism based on the model proposed by Bozzelli et al.[24] enabled us to assess the role played by radicals such as ClO and OH in the degradation processes of CH_2Cl_2, and in particular their respective role in the evolution of the CO concentration as a function of temperature and residence time. Analysis of reaction fluxes shows that the oxidation of CO to CO_2 by ClO radicals is the dominant pathway at temperatures lower than 1000 K under our operating conditions (large air excess). The same results indicate that at higher temperatures, the oxidation of CO to CO_2 by OH radicals becomes predominant. A similar analysis of elementary processes responsible for the conversion of CO to CO_2 has also been performed[25] for the thermal oxidation of 1,3-hexachlorobutadiene (1,3-C_4Cl_6) under fuel lean conditions (1000 ppm v/v in 1 atm of air). In this case, the CO + ClO → CO_2 + Cl reaction was found to be the most important pathway in the oxidation of CO into CO_2 over the whole temperature range (compared to the two other possible CO oxidation processes: CO + O_2 → CO_2 + O and CO + O + M → CO_2 + M). Therefore, our results show that although the rate constant of the CO + ClO → CO_2 + Cl reaction is consistently lower than the one of the CO + OH → CO_2 + H reaction over a wide temperature range ($k_{CO+OH}/k_{CO+ClO} \sim 200$ at 1000 K and $k_{CO+OH}/k_{CO+ClO} \sim 3.75$ at 2500 K), the relative importance of these two processes in the oxidation of CO also depends on the concentrations of ClO and OH radicals generated under operating conditions. Excess air (fuel lean conditions), low temperatures and a low content of H atoms in the chemical composition of the chlorinated species favor the oxidation of CO to CO_2 by ClO radicals in their thermal processes of oxidative degradation. Our results suggest the need for direct measurements of ClO radicals under combustion conditions in order to assess the importance of the ClO radicals in the CO → CO_2 oxidation process.

Conclusion

Ab initio electronic structure calculations, combined with canonical transition state theory, carried out on the oxidation reaction of CO by ClO radicals, lead to the conclusion that the addition of ClO to CO is the rate-determining step, characterized by lower rate constants than those obtained for the reaction of OH + CO → H + CO_2. The relative importance of these reaction pathways to convert CO into CO_2 in the thermal degradation processes of chlorinated species depends on the concentration of ClO and OH radicals generated under the operating conditions. Our results indicate that despite the relative low rate constants for the ClO + CO reaction (as compared to CO + OH), this reaction becomes the dominant pathway in the oxidation of CO in combustion processes characterized by excess air, relatively low temperatures and a low content of hydrogen atoms in the chemical composition of the chlorinated species involved in the combustion process.

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