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Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 201–205

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photochemistry of the gaseous hydrogen peroxide–carbon monoxide system

III. Calculated energetics for possible HO_2–CO complexes

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Received 15 April 1994; accepted 28 June 1994

Abstract

At 298 K, HO_2 radicals formed by secondary reactions in the photochemistry of the H_2O_2–CO system do not react with CO, whereas OH radicals formed in the primary process do. To explain the non-reactivity of HO_2, we made Hartree–Fock calculations of the energies needed to form three probable HO_2–CO intermediate radical complexes: **I**, $HOO\dot{C}{=}O$; **II**, **III**. The values of ΔE for the reaction $HO_2+CO \rightarrow R$ and $\Delta H_f°$ for R obtained at 298 K are as follows:

	R				
	I	**II** sym)	**II** (anti)	**III** (syn)	**III** anti)
ΔE (kJ)	89	6	9	−280	−259
$\Delta H°$ (kJ mol^{-1})	−22	−105	−102	−391	−370

From the high-temperature rate data, we conclude that the first stage of the reaction is the formation of complex **I** with ΔE the same or almost the same as the activation energy for the reaction to yield products CO_2 and OH, and that every collision of the reactants with sufficient energy yields the complex.

Keywords: Hydrogen peroxide–carbon monoxide; Energetics; HO_2–CO complexes

1. Introduction

In the presence of oxygen, HO_2 (hydroperoxo) is formed during H_2O_2–CO photolysis by the sequence [1,2]

$$H_2O_2+h\nu\ (254\ \text{nm}) \longrightarrow 2OH \qquad \Delta H°(n_{h\nu}=0)=214\ \text{kJ [3]} \tag{1}$$

$$OH+H_2O_2 \longrightarrow H_2O+HO_2 \quad \Delta H° = -143\ \text{kJ} \tag{2}$$

$$OH+CO \longrightarrow CO_2+H \quad \Delta H° = -104\ \text{kJ} \tag{3}$$

$$H+O_2+M \longrightarrow HO_2+M \quad \Delta H° = -216\ \text{kJ} \tag{4}$$

$$2HO_2 \longrightarrow H_2O_2+O_2 \quad \Delta H° = -140\ \text{kJ} \tag{5}$$

In the absence of oxygen, the reaction

$$H+H_2O_2 \longrightarrow H_2+HO_2 \quad \Delta G° = -80\ \text{kJ} \tag{6}$$

may occur, but no H_2 is found when oxygen (a few Torr) is present in the system. In the troposphere the concentration of OH is some 10^5–10^7 cm^{-3} depending on conditions [4], and OH can yield HO_2 in the atmosphere by the above sequence. CO and NO are important constituents of polluted atmospheres as both derive from the combustion of fossil fuels. Hence the following reactions are considered

$$HO_2+CO \longrightarrow CO_2+OH \quad \Delta H° = -246.1\ \text{kJ} \tag{7}$$

$$HO_2+NO \longrightarrow NO_2+OH \quad \Delta H° = -20.3\ \text{kJ} \tag{8}$$

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SDI 1010-6030(94)03916-I

The above simplified scheme excludes a number of other sources of OH and HO_2 and other pollutants, but is sufficient for our purpose. Comprehensive considerations are to be found in Ref. [5].

A fundamental tenet of contemporary atmospheric chemistry is that reactions (3) and (8) are very important and reaction (7) is negligibly slow. For reaction (8), the evaluated rate constant [6] is given as $k_8 = 8.3 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Some time ago, on the basis of the results of Baldwin et al. [7] on the relative rates of reaction of HO_2 with CO and H_2 at 773 K, we estimated that, at 298 K, $k_7 \approx 10^{-22}$–10^{-28} cm^3 $molecule^{-1}$ s^{-1} [1]. The spread comes from the range of possible steric factors from 10^{-6} ($k_7 \approx 10^{-22}$) to unity ($k_7 \approx 10^{-28}$). (To some researchers used to seeing higher steric factors associated with higher rate constants this may seem a paradox, but it originates from our treatment. Knowing the rate constant at only a single temperature, 773 K, neither the Arrhenius parameter A nor E is known. To estimate the rate constant at 298 K, we assume values of A. For each A value to yield the same value of k at 773 K, the accompanying value of E increases with increasing A and hence yields a more negative exponent in the Arrhenius exponential. This leads to a greater rate for a decrease in k with decreasing temperature.) While our paper was in press, the results of an electron spin resonance (ESR) kinetic spectroscopy study claimed that $k_7 \approx k_3$ (above 10^{-13}) at 298 K [8]. On the basis of experimental work (competitive kinetics) by three independent groups, this claim was soon unequivocally shown to be in error by many orders of magnitude [9–11]. More recently, Atri et al. [12], from results of thermal reactions in CO–H_2–O_2–N_2 mixtures at 773 K, combined with results of Baldwin et al. [13] at 713 K, reported Arrhenius parameters for k_7 of $A = 5.8 \times 10^{10}$ l mol^{-1} s^{-1} and $E_a = 96.0$ kJ mol^{-1} based on the relative rates of reaction of HO_2 with CO and with HO_2 (reaction (5)). An extrapolation of the resulting Arrhenius expression, $k_7 = 9.6 \times 10^{-11} \exp(-1.15 \times 10^4/T)$ cm^3 $molecule^{-1}$ s^{-1}, yields $k_7 = 1.7 \times 10^{-27}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. Confidence in their 773 K value was reinforced by the determination in the same system of a value for k_3 based on the relative rates of reaction of OH with CO and H_2 from which they obtained $k_3 = 1.6 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 773 K, in reasonable agreement with a representation of several determinations of this rate constant [14]. Although the extrapolation of the simple Arrhenius expression over such a wide range is not expected to yield an accurate rate constant, the error is not expected to be more than a factor of ten, or $k_7 = 1.7 \times 10^{-27} \times 10^{\pm 1}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. This value is in accord with our low end estimate, based on a steric factor near unity, which the Arrhenius expression $A = 9.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} indicates.

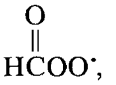
The high activation energy for the reaction, and hence its slowness, is unexpected because it bears a resemblance to the reaction of OH with CO, $k_3 = 10^{-13}\{1 + (0.59 \pm 0.10P)\}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K with P in atmospheres [15], and both reactions have negative ΔH. Therefore the OH model seems an appropriate guide for the development of a model for HO_2.

1.1. The hydroxyl–carbon monoxide model

Hynes et al. [15] list some 40 studies of reaction (3) from 1964 to 1985. The principal mechanistic features are mostly well understood and continuing theoretical [14] and combined experimental and theoretical [16,17] work has elucidated the fine detail. The reaction proceeds through the formation of an intermediate radical complex with excess energy

$$\mathrm{OH + CO \longrightarrow HO\dot{C}O^*} \qquad (9)$$

(trans minimum, $\Delta H = -155$ kJ mol^{-1}; cis minimum, $\Delta H = -145$ kJ mol^{-1} [14]; $k_9 = (1.0 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} [16]; about seven times faster than k_3). The conclusion is that the complex may undergo a back reaction or yield the products CO_2 and H. The back reaction may be slowed by collisional deactivation of the complex, accounting for the increase in k_3 with pressure. By analogy with this model, invoking complex formation for the HO_2–CO reaction gives three possible isomeric free radical complexes: **I**, $\mathrm{HOO\dot{C}{=}O}$, hydroperoxooxomethyl; **II**, oxomethyldioxy; **III**, hydroxyoxomethoxy. In the following, the energies for the formation of these complexes from $CO + HO_2$ are calculated.



$\mathrm{HC(=O)OO^{\bullet}}$,

II

$\mathrm{HOC(=O)O^{\bullet}}$

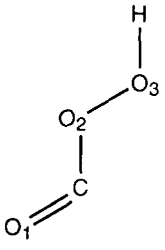
III

2. Theoretical studies

In spite of its obvious importance, practically nothing is known about the $HCO_3^{\bullet}$ free radical in isomeric forms **I** and **III**. Francisco and Williams [18] have investigated form **II** by ab initio methods. Semi-empirical studies include work on $CO_3H^{\bullet}$ (structure otherwise unspecified) by the MINDO/2 method [19], and work on isomer **III** by the CNDO/2 method [20].

We have undertaken a series of ab initio studies of isomer **I** (both planar and non-planar) and isomer **III** (planar, in both syn and anti forms). We used standard ab initio methods. The gaussian series of programs [21] was used throughout. The molecular geometry was specified by the Z-matrix approach. Standard keyword choices were used to select methods and options. The basis set was the 6-31G* set of gaussian functions. The molecular geometry was determined by the unrestricted Hartree–Fock (UHF) technique with an analytical gradient method. Analytical second derivatives of the UHF wavefunction were used to determine the harmonic vibrational frequencies.

We have studied the chain isomer I in two forms: a planar form **1** of higher energy and a non-planar form **2** of lower energy. The planar form has one imaginary out-of-plane vibrational frequency, and hence it is really a transition state between two equivalent non-planar forms. Table 1 lists the properties of both forms (note that the OCOO moiety of the non-planar form is almost planar (torsion angle, 178.0°)).



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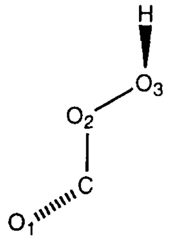

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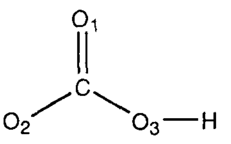
The planar "bicarbonate" isomer III has two forms: the syn form **3** with the hydroxyl and carbonyl groups on the same side of the C–O_3 bond, and the anti form **4** in which they are on opposite sides. For each structure, all vibrational frequencies are real, so there is no tendency towards non-planarity. (Several attempts to find a non-planar energy minimum were fruitless.) Table 2 summarizes the properties of each structure.



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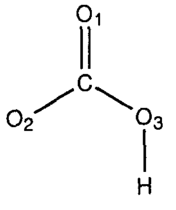

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Table 1
Properties of the HOOĊ=O radical [a]

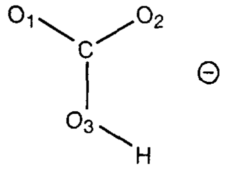
Property	Planar, C_s, **1**	Non-planar, C_1, **2**
$r_e(CO_1)$	1.161	1.160
$r_e(CO_2)$	1.326	1.330
$r_e(O_2O_3)$	1.399	1.393
$r_e(O_3H)$	0.951	0.952
$\theta_e(O_1CO_2)$	126.2	126.1
$\theta_e(CO_2O_3)$	108.8	109.8
$\theta_e(O_2O_3H)$	100.0	101.4
$\theta_e(O_1CO_2O_3)$	180.0	178.0
$\theta_e(HO_3O_2C)$	180.0	122.7
Energy, SCF	90.4	88.8
Dipole moment	3.25	3.16

[a] Bond lengths in ångströms, angles in degrees, energies in kilojoules per mole relative to $CO+HO_2$ and dipole moments in debye.

Table 2
Properties of the $\mathrm{HO\overset{\overset{O}{\|}}{C}O^{\bullet}}$ radical

Property	syn, C_s, **3**	anti, C_s, **4**
$r_e(CO_1)$	1.180	1.172
$r_e(CO_2)$	1.324	1.335
$r_e(CO_3)$	1.313	1.318
$r_e(O_3H)$	0.952	0.951
$\theta_e(O_1CO_2)$	123.0	122.6
$\theta_e(O_3CO_1)$	127.5	125.8
$\theta_e(CO_3H)$	108.5	113.1
Energy, SCF	−280.1	−259.4
Dipole moment	2.27	3.71

It is somewhat surprising that these structures have such clearly identifiable carbonyl bonds, much shorter than the C–O single bonds, when the planar carbonate anion (CO_3^{2-}) has three equal C–O bond lengths and the planar bicarbonate anion (HCO_3^-) (**5**) has two almost equal C–O bond lengths. With a 6-31G* basis set and the restricted Hartree–Fock (RHF) method, we obtained bond lengths of 1.219 Å for C–O_1 and the slightly larger value of 1.234 Å for C–O_2. (The O_1CO_3 and O_2CO_3 angles are likewise almost equal: 114.5° and 113.5° respectively.) The equality of bond lengths in these anions is typically explained as a resonance phenomenon.



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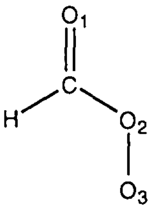
However, when we used the bicarbonate anion geometry for the bicarbonate radical, the energy was 87.4 kJ mol^{-1} higher than the energy of the syn structure. What is the origin of this difference? From a molecular orbital point of view, we have removed an electron of HCO_3^- from the 3a″ highest occupied molecular orbital (HOMO). (As the structure optimizes and the bond lengths become increasingly different, there is a reordering of orbital energies such that, for both the syn and anti structures, the singly occupied MO has a′ symmetry. However, this shift does not affect the argument here.) Examination of the 3a″ orbital of HCO_3^- shows that it primarily describes an out-of-plane lone pair on O_1 and O_2. Since the removal of one of these lone pair electrons causes the molecular geometry to change to one with unequal bond lengths, we may conclude that it is these lone pair electrons that are enforcing bond length equality. This molecular orbital point of view places enhanced emphasis on the role of lone pair interactions compared with the standard valence bond explanation which emphasizes the role of bonding electrons.

For completeness, Table 3 summarizes the results of Francisco and Williams [18] for isomeric form **II**, formed during the oxidation of formyl in a low-temperature matrix [22], using the UHF method and a 6-31G* basis set. They found both a syn structure **6** and an anti structure **7**.



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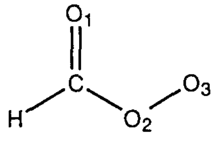

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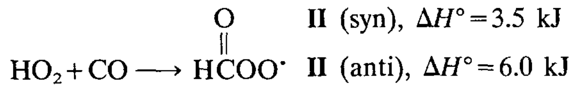
Finally, we note that the energy difference between (HO_2+CO) and $(OH+CO_2)$ differs substantially from the JANAF value (calculated, 283.7 kJ mol^{-1}; JANAF, 246.1 kJ mol^{-1} [3]). With more accurate configuration interaction (CI) energies, the error should decrease significantly.

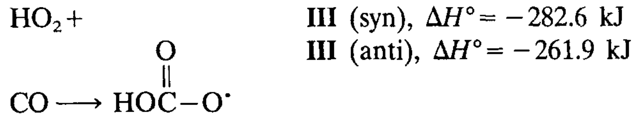
3. Results and discussion

The calculations yield

$$HO_2+CO \longrightarrow HOO\dot{C}{=}O \quad \mathbf{I},\ \Delta H^\circ = 86.3\ \text{kJ} \qquad (10)$$



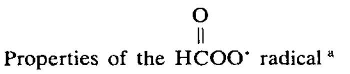
$$HO_2+CO \longrightarrow H\overset{\overset{\displaystyle O}{\|}}{C}OO^{\bullet} \quad \begin{matrix}\mathbf{II}\ (\text{syn}),\ \Delta H^\circ = 3.5\ \text{kJ}\\ \mathbf{II}\ (\text{anti}),\ \Delta H^\circ = 6.0\ \text{kJ}\end{matrix} \qquad (11)$$



$$HO_2 + CO \longrightarrow HO\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{\bullet} \quad \begin{matrix}\mathbf{III}\ (\text{syn}),\ \Delta H^\circ = -282.6\ \text{kJ}\\ \mathbf{III}\ (\text{anti}),\ \Delta H^\circ = -261.9\ \text{kJ}\end{matrix} \qquad (12)$$

From these values of ΔH°, the calculated values of the enthalpies of formation (kJ mol^{-1}) at 298 K are as follows: **I**, −22.1; **II** (syn), −104.9; **II** (anti), −102.0; **III** (syn), −391.0; **III** (anti), −370.3. A value of ΔH_f° for **III** of −418 kJ mol^{-1} has been reported [19]; however, this calculation appears to be meaningless since the same paper gives ΔH_f° for HO_2 as −409 kJ mol^{-1}, whereas JANAF [3] gives 2.1±8.4 kJ mol^{-1}; values listed for a number of other radicals are also impossible.

Table 3



Properties of the $H\overset{\overset{\displaystyle O}{\|}}{C}OO^{\bullet}$ radical [a]

Property	syn, C_s, **6**	anti, C_s, **7**
$r_e(CO_1)$	1.167	1.168
$r_e(CO_2)$	1.370	1.364
$r_e(O_2O_3)$	1.313	1.318
$r_e(CH)$	1.083	1.083
$\theta_e(HCO_1)$	127.7	126.9
$\theta_e(HCO_2)$	111.7	107.1
$\theta_e(CO_2O_3)$	111.2	113.7
Energy, SCF	6.0	8.5

[a] Data from Ref. [18].

The energy level reaction profile, shown in Fig. 1, gives values for the ground state complexes relative to HO_2+CO as zero; only the lower level (syn) values are shown for complexes **II** and **III**. Transition state energies have not been calculated. In view of the discrepancy noted at the end of Section 2 between the calculated and JANAF [3] values of the difference between the energies of the initial reactants (HO_2 and CO) and the final products (HO and CO_2), we expect that with the application of more sophisticated theory (CI energies) the difference should decrease. We leave this for the future at which time we should be able to calculate the transition state energies with some confidence.

Complexes **II** and **III** are thermochemically favored; however, the formation of either requires an improbable rearrangement, whereas the formation of **I** is a straightforward addition. The experimental [13] *A* factor is about at collisional frequency and hence is much higher than would be expected for a mechanism involving rearrangement, but not for addition. Moreover, ΔE for the formation of **I**, although not necessarily the activation energy, is calculated to be near the experimental E_a value. We conclude that complex **I** is formed at or

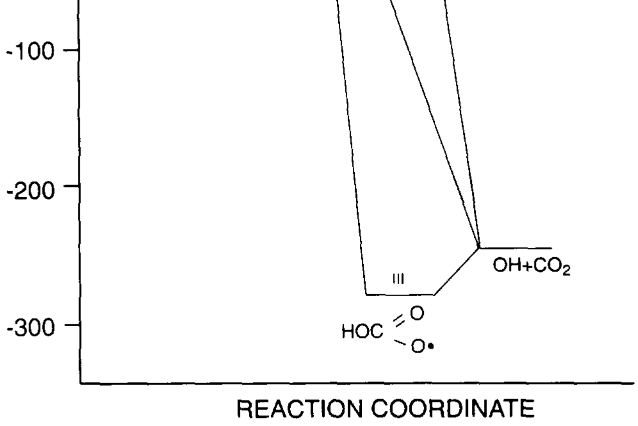


Fig. 1. HO_2+CO reaction profile. Energies of lowest radical state.

near the collisional frequency provided that there is sufficient energy and that this is the rate-determining step. On this basis **I** can undergo a rapid unimolecular reaction either to an intermediate radical, **II** or **III**, or directly to products $OH + CO_2$. In the absence of more information at this time, it seems best to suggest that the direct formation of the products from complex **I** is the most probable since it does not require a prior internal reorganization.

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