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Photochemistry of the gaseous hydrogen peroxide–carbon monoxide system

IV. Survey of the rate constant and reaction profile for the $HO_2 + CO \rightarrow CO_2 + OH$ reaction

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Abstract

This survey begins with the photochemistry at 254 nm and 298 K in the system H_2O_2–CO–O_2–RH, the primary objective of which is to determine the rate constants for the reaction $OH + RH \rightarrow H_2O + R$ relative to the well-known rate constant for the reaction $OH + CO \rightarrow CO_2 + H$. Inherent in the scheme is that the reaction $HO_2 + CO \rightarrow OH + CO_2$ is negligible compared with the OH reaction, and a literature consensus gives $k_{HO_2} < 10^{-19}$ cm^3 molecule^{-1} s^{-1}, or some 10^6 less than k_{OH} at 298 K. Theoretical calculations establish that the first stage in the HO_2 reaction is the formation of a free radical intermediate $HO_2 + CO \rightarrow HOO\dot{C}O$ (perhydroxooxomethyl) which decomposes to yield the products, and that the rate of formation of the intermediate is equal to the rate of formation of the products. The structure of the intermediate and a reaction profile are shown.

High temperature rate data reported subsequent to the data in the consensus and theoretical calculations lead here to a recommendation that, in the range 250–800 K, $k_{HO_2} = 3.45 \times 10^{-12} T^{1/2} \exp(1.15 \times 10^4/T)$ cm^3 molecule^{-1} s^{-1}, the hard-sphere-collision Arrhenius modification. This yields $k_{HO_2(298)} = 1.0 \times 10^{-27}$ cm^3 molecule^{-1} s^{-1} or some 10^{14} slower than $k_{OH(298)}$.

Keywords: Hydrogen peroxide–carbon monoxide system; Photochemistry; Rate constant; Reaction profile

1. Introduction

In the first volume of the *Journal of Photochemistry*, we published a paper on the photochemistry of the hydrogen peroxide–carbon monoxide system [1]. The objective of this work was to obtain rate constants for H-atom abstraction by OH using a scheme of competitive kinetics of OH with CO to yield CO_2. Inherent in the scheme was that the rate of reaction of HO_2 with CO was several orders of magnitude less than that of OH with CO. Thus began my interest in the HO_2–CO reaction. A survey seemed particularly appropriate for this anniversary, since the article began on page 1 of the first issue of the *Journal of Photochemistry*. Although at the end this excursion is computer driven, its start for me begins almost half a century ago with the gas-phase photolysis of H_2O_2 [2].

Since this survey recapitulates our published work, many literature sources are not cited herein. These may be found together with expanded discussions in the cited references.

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1.1. Photolysis-initiated scheme and variations

The photolysis of H_2O_2 at 298 K and 254 nm is given by

$$H_2O_2 + h\nu(254\ \text{nm}) \rightarrow 2OH \qquad (1)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (2)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (3)$$

independent of added gases, N_2, O_2 and H_2O [2]. However, in the presence of CO at pressures high relative to that of H_2O_2, the reaction

$$OH + CO \rightarrow CO_2 + H \quad \Delta H^\circ = -104\ \text{kJ} \qquad (4)$$

predominates. With sufficient added O_2, H atoms are removed by

$$H + O_2 + M \rightarrow HO_2 + M \qquad (5)$$

In the presence of a molecule with an abstractable H atom (RH), there is competition for OH between reaction (4) and

$$OH + RH \rightarrow H_2O + R \qquad (6)$$

From these equations, the appropriate rate expressions and steady state approximations, we obtained ratios for k_6/k_4 and k_2/k_4 based on the rate of CO_2 formation and relative rate constants for the reaction of OH with H_2O_2 and for several hydrocarbons. We have described these mechanisms and rate studies in considerable detail in earlier articles [1,3].

1.2. Rate of the HO_2–CO reaction at 298 K: experiments and extrapolations

Before initiating the above studies, we realized that if the reaction of HO_2 with CO

$$HO_2 + CO \rightarrow CO_2 + OH \quad \Delta H^\circ = -246 \text{ kJ} \tag{7}$$

was appreciable, our scheme would not be applicable. The reaction had sometimes been assumed to be fast, presumably because of its resemblance to reaction (4) and its high exothermicity [4]. However, from high temperature rate data and a relative rate constant at a single temperature (500 °C) [5], we estimated that k_7 was in the range 10^{-28}–10^{-22} cm^3 molecule^{-1} s^{-1} at 298 K [1], clearly not competitive with the then recommended $k_4 = (1.5 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

At the time that our work was in press, from gas-phase kinetic spectroscopy (electron spin resonance, ESR), a relative rate constant for k_7 equivalent to a value of about k_4 was reported [6]. In rebuttal, we published experimental results which showed that k_7 had to be less than about $10^{-3}k_4$ [7]. Our report was soon followed by reports from two other groups [8,9] which agreed that $k_7 < 10^{-6}k_4$. These reports were motivated by considerations of the implication that a fast k_7 value would have for the models of air pollution. At the time, the early 1970s, it was being recognized that the ambient concentration of OH in the atmosphere was roughly 10^6 cm^{-3} and that reaction (4) accounted for the removal of CO, hitherto considered inert, from contaminated air. If $k_7 \cong k_4$, reactions (4) and (7) would constitute a chain for CO conversion to CO_2, and reactions of HO_2 with other components, NO in particular, could not occur. A survey consensus gave $k_7 < 10^{-19}$ cm^3 molecule^{-1} s^{-1} at 300 K [10] based on the data of the two groups [8,9]. During this period, Atri et al. [11] from results of thermal reactions in CO–H_2–O_2–N_2 mixtures at 773 K and 713 K, reported Arrhenius parameters yielding $k_7 = 9.6 \times 10^{-11} \exp(-1.15 \times 10^4/T)$ cm^3 molecule^{-1} s^{-1}. Assuming constant Arrhenius parameters A and E_a, this yields $k_7 = 1.7 \times 10^{-27}$ cm^3 molecule^{-1} s^{-1} at 298 K, not far from the low end of our estimate [1].

2. The $HO_2 + CO$ reaction: theory and mechanism

After a hiatus of over 20 years during which time we are unaware of any significant developments, we returned to the HO_2–CO reaction [12,13]. In part, the impetus was the work of various groups [14–16] in elucidating the involvement of the HOCO intermediate complex in the HO + CO reaction, particularly the elegant experimental work of the Birmingham group [14].

For the HO_2–CO reaction, we consider three possible isomeric free radical complexes: **I**, $HOO\dot{C}{=}O$, hydroperoxooxomethyl; **II**, $HC{=}OOO^{\cdot}$, oxomethyldioxy; **III**, $HOC{=}OO^{\cdot}$, hydroxyoxomethoxy [12]. Radical **II**, a possible intermediate in the reaction of formyl radical with O_2, had been investigated by ab initio methods [17]. Using standard ab initio methods, we made calculations on isomer **I** (both planar and non-planar) and isomer **III** (planar, in both syn and anti forms). From these calculations, we concluded that radical complex **I** was formed as an intermediate in the CO_2–HO_2 reaction and that the radical yielded the products

$$HO_2 + CO \rightarrow HOO\dot{C}{=}O \tag{8}$$

$$HOO\dot{C}{=}O \rightarrow HO + CO_2 \tag{9}$$

Although we believed the calculations were sufficient to establish this argument, there was considerable discrepancy between the value of ΔH° for reaction (7) calculated by us and that calculated from JANAF thermochemical tables. Hence we deferred further calculations, such as transition state energies, until we were able to apply more accurate configuration interaction (CI) energies.

We have now carried out these calculations [13]. At optimized unrestricted Hartree–Fock (UHF) geometries, we obtained configuration interaction wavefunctions (CISD); additionally, size correction was used to calculate the energetic effects of unlinked quadrupole excitations. For reaction (7), we thus obtained $\Delta H^\circ = -242.7$ kJ mol^{-1}, now in excellent agreement with the -246.1 ± 8.4 kJ obtained from JANAF tables. This reinforces confidence in the calculations.

The calculated structure of the intermediate $HOO\dot{C}{=}O$ formed in reaction (8) is shown in Fig. 1. Relative to $HO_2 + CO$ at zero, E for this radical complex is 48.5 kJ mol^{-1}; hence, for reaction (8), $\Delta H^\circ_{8(298)} = 46.0$ kJ and the enthalpy of formation of the intermediate $\Delta H^\circ_{f(298)} = -62.4$ kJ mol^{-1}. For the transition state (TS1) for reaction (8), $E = 92.9$ kJ mol^{-1}. For the transition state (TS2) for reaction

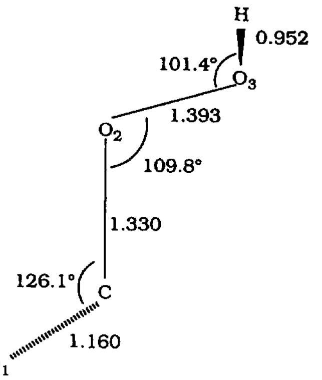

Fig. 1. The $HOO\dot{C}{=}O$ (hydroperoxooxomethyl) radical intermediate. Torsion angles: HO_3O_2C, 122.7°; $O_1CO_2O_3$, 178.0°. Bond lengths in angstroms. (Reprinted with permission from Ref. [13]. Copyright 1996 American Chemical Society.)

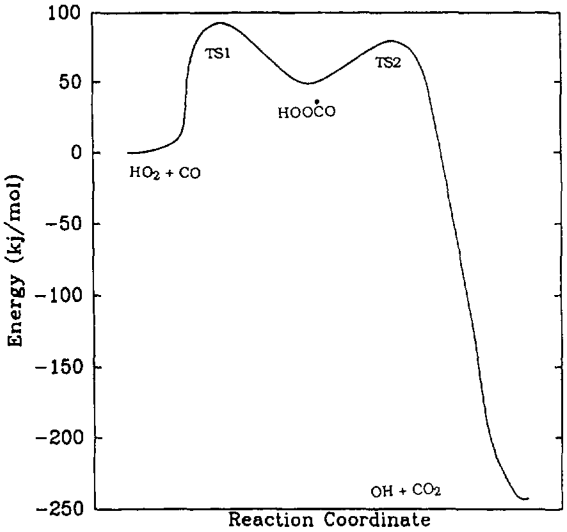

Fig. 2. Reaction profile across the radical potential energy surface. (Reprinted with permission from Ref. [13]. Copyright 1996 American Chemical Society.)

(9), $E = 79.8$ kJ mol^{-1}. The calculated structures for the two transition states, dipole moments and vibrational frequencies are given in Ref. [13]. The calculated reaction profile is shown in Fig. 2.

3. Conclusions

Reaction (7) of HO_2 is a two-step process: formation of an intermediate $HOO\dot{C}{=}O$, followed by decomposition of the intermediate (reactions (8) and (9)). The calculated activation energy for reaction (8), the energy of TS1, is 92.9 kJ mol^{-1}. For reaction (9), E at TS2, 79.8 kJ mol^{-1}, combined with the ground state energy of the intermediate, 48.5 kJ mol^{-1}, yields an activation energy of 31.3 kJ mol^{-1} for the reaction. This barrier is well below the energy liberated from TS1 to the ground state, 44.4 kJ mol^{-1}.

Our calculated activation energy, 92.9 kJ mol^{-1}, for reaction (8) is in good agreement with the experimental value of 96.0 kJ mol^{-1} derived from high temperature rate data for reaction (7) [11]. Hence only TS1 contributes to the activation energy from reactants to products. The experimental pre-exponential Arrhenius parameter A indicates that there is no steric barrier to reaction. The agreement between theory and experiment for the activation energy adds considerably to an acceptance of the Arrhenius parameters given by Atri et al. [11]. Their A factor is not distinguishable from that which hard-sphere collision theory would yield. Such a theory includes a $T^{1/2}$ factor for collision frequencies. For these reasons, the recommended rate constant in the range 250–800 K is $k_7 = 3.45\times10^{-12}T^{1/2}\exp(-1.15\times10^4/T)$ cm^3 molecule^{-1} s^{-1}. At 298 K, this gives $k_7 = 1.03\times10^{-27}$ rather than the $k_7 = 1.7\times10^{-23}$ cm^3 molecule^{-1} s^{-1} obtained keeping the Arrhenius parameter A constant. It is possible that a better value may be forthcoming from relative rate studies, but it is unlikely that such studies will yield a significantly better or more useful rate constant. Presumably a more definitive value will depend on direct, rather than relative, but still unreported experimental determinations.

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