Research paper

Kinetics and mechanism of the reaction of recombination of vinyl and hydroxyl radicals

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ABSTRACT

The recombination of the vinyl (C_2H_3) and the hydroxyl (OH) radicals was studied computationally using quantum chemistry and master equation/RRKM. The reaction mechanism includes the initial addition, several isomerization steps, and decomposition via seven different channels. The spectrum of products demonstrates temperature dependence in the 300–3000 K range. At low temperatures (below 1600 K), CH_3 + HCO products are dominant but at elevated temperatures vinoxy radical (CH_2CHO) and hydrogen atom become more important. The acetyl (CH_3CO) + H products and formation of vinylidene (CH_2C:) and water products are minor but non-negligible.

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1. Introduction

Vinyl and hydroxyl radicals are universally recognized as important intermediates in the processes of hydrocarbon oxidation and combustion. Reactions of C_2H_3 and OH influence both the rates and the products of the overall combustion process; both species reach high concentrations in certain regions of hydrocarbon flames. Although properties of many reactions of these intermediates are now known with high degree of certainty due to experimental and theoretical work by many groups, the kinetics of the radical-radical reaction between vinyl and OH is largely unknown.

No experimental data on this reaction are currently available. Neither the rate constant of the overall reaction nor the product distribution are known. The only information on the rate constant of the reaction between vinyl and hydroxyl available in the literature is the 1986 recommendation by Tsang and Hampson [1] for the rate constant of the disproportionation channel producing the C_2H_2 + H_2O products (5×10^{-11} cm³ molecule⁻¹ s⁻¹). This recommended value of the rate constant is included in a number of combustion models. However, the recombination channel (reaction 1), which can be expected to be followed by chemically activated isomerization and decomposition of the C_2H_4O adduct, is generally ignored in chemical models of hydrocarbon combustion.

$$C_2H_3 + OH \rightarrow Adduct \rightarrow Products \qquad (1)$$

The mechanism of the C_2H_3 + OH recombination is expected to involve the initial formation of the vinyl alcohol adduct, which can isomerize into acetaldehyde; both of these species can decompose to form a variety of products. The potential energy surfaces (PESs) of decomposition and isomerization of acetaldehyde and vinyl alcohol have been characterized in a number of publications (e.g., [2,3] and references therein) and the kinetics and the products of acetaldehyde thermal decomposition have been studied both experimentally and theoretically (e.g., [2,4–6] and references therein). However, no theoretical values of the rates and the product branching ratios of reaction 1 have been published.

In 2002, Liu et al. [6] studied the PES of the C_2H_4O potential energy surface with the purpose of analyzing the mechanism of reaction 1. These authors used the QCISD(T)/6-311G(2df,p)//B3LYP/6-311G(d,p)-level calculations to investigate potential channels of the reaction. To this day, this work remains the most comprehensive in terms of pathways to product formation. In addition to the vinyl alcohol adduct and acetaldehyde, the authors studied the pathways of formation and transformation of several other higher-energy C_2H_4O isomers, including two (cis-CH_3COH and trans-CH_3COH) that affect the composition of the reaction products. However, the PES information obtained in [6] was not used by the authors to model the kinetics of the adduct transformations and the final product distributions. The authors of this study concluded that the CH_2CO + H_2 and the CH_3CO + H product sets are likely to be dominant in reaction 1.

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In the current work, the PES of reaction 1 was studied using quantum chemistry. A master equation model was created on the basis of the PES study, RRKM calculations, and Inverse Laplace Transform analysis of the rate constants for barrierless product channels. The model was used to evaluate product branching over a wide range of temperatures and pressures. The results of the PES study are very similar to those reported by Lui et al. [6] but the predicted distribution of products is significantly different, as described below.

2. Potential Energy Surface (PES)

Molecular structures were optimized using the density functional BH&HLYP method [7,8] with the aug-cc-pVDZ basis set [9] and vibrational frequencies were calculated for all PES stationary points using the same technique. The CCSD(T) method [10,11] was used for single-point energy calculations for all stationary points. The aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets were used; complete basis set (CBS) extrapolation was performed using the method of [12]. The Gaussian 09 program [13] was employed in all potential energy surface calculations. The version of the BH&HLYP functional implemented in Gaussian 09 was used which, as described in the Gaussian manual, is different from that of [7,8].
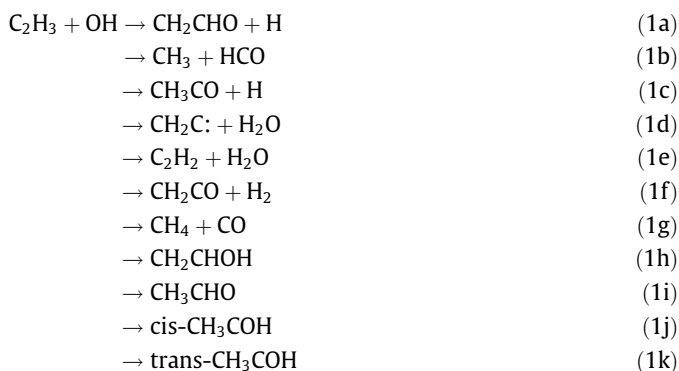
The reaction PES is displayed in Fig. 1. Initial C_2H_3 + OH addition and subsequent isomerization processes are shown with solid lines, channels of decomposition via energy barriers are shown with dashed lines, and those of barrierless decomposition – with dotted lines. The vinyl alcohol adduct (CH_2CHOH) can undergo isomerization to acetaldehyde (CH_3CHO, lowest energy pathway) or biradical CH_3COH species (trans or cis), or undergo decomposition via one of the three channels: vinylidene (CH_2C:) + H_2O, acetylene (C_2H_2) + H_2O, or vinoxy radical (CH_2CHO) + H. Acetaldehyde can undergo isomerization back to vinyl alcohol or to trans-CH_3COH, or decomposition to one of the two sets of molecular products (CH_2CO + H_2 and CH_4 + CO, tight [14] transition states) or one of the three radical product sets (CH_3 + HCO, CH_3CO + H, or CH_2-COH + H, barrierless transition states).

The two isomers of CH_3COH can interconvert via internal rotation about the C—O bond (with a barrier of 102 kJ mol^{-1}; all energies quoted henceforth include vibrational zero-point energy, ZPE, unless otherwise specified), or decompose to form the acetyl radical (CH_3CO) and the H atom. Decomposition of the trans-CH_3COH isomer requires overcoming a barrier and thus has a tight transi-

tion state. Geometry optimization performed using the density functional BH&HLYP method finds a small barrier for the decomposition of the cis-CH_3COH isomer (3.3 kJ mol^{-1} relative to CH_3CO + H). However, subsequent single-point CBS energy calculation reduces the barrier to below the product asymptote (-8.8 kJ mol^{-1} relative to CH_3CO + H). Any conformation of the C_2H_4O adduct can also be stabilized via collisions with the bath gas.

A number of processes that can occur on the C_2H_4O PES are not shown in Fig. 1 as they are not relevant to the reaction in question. This includes isomerization to oxirane (ethylene oxide), which has no competitive channels of decomposition that do not proceed through CH_2CHOH or CH_3CHO [15]. Also, decomposition of cis-CH_3COH to CH_4 + CO, trans-CH_3COH to CH_2C: + H_2O, and formation and decomposition of the CH_3OCH species have energy barriers that are too high to be important [6].

The resultant list of all possible product channels is as follows:

$$C_2H_3 + OH \rightarrow CH_2CHO + H \tag{1a}$$
$$\rightarrow CH_3 + HCO \tag{1b}$$
$$\rightarrow CH_3CO + H \tag{1c}$$
$$\rightarrow CH_2C: + H_2O \tag{1d}$$
$$\rightarrow C_2H_2 + H_2O \tag{1e}$$
$$\rightarrow CH_2CO + H_2 \tag{1f}$$
$$\rightarrow CH_4 + CO \tag{1g}$$
$$\rightarrow CH_2CHOH \tag{1h}$$
$$\rightarrow CH_3CHO \tag{1i}$$
$$\rightarrow cis\text{-}CH_3COH \tag{1j}$$
$$\rightarrow trans\text{-}CH_3COH \tag{1k}$$

3. Energy-dependent rate constants

For the sake of convenience in describing individual processes occurring on the reaction PES, the reactants, all potential energy wells, and all product sets of reaction 1 are numbered (Fig. 1 and Table S2 in the Supporting material). Henceforth, individual transformations (isomerizations, additions, decompositions) and their energy-dependent rate constants are identified by double indices, where the first and the second index correspond to the starting and the ending species of the process (e.g., isomerization 1,2 and $k_{1,2}(E)$ for the isomerization of the CH_2CHOH adduct to CH_3CHO).

Energy dependent rate constants were calculated for all processes involving distinct energy barriers using the RRKM method [16] with the barrier-width based Eckart tunneling correction [17,18] and the transition state properties obtained in quantum chemical calculations; the ChemRate program [19] was used in these calculations. For the barrierless channels of decomposition to form free radicals, Inverse Laplace Transform (ILT) [20] of the corresponding high-pressure-limit Arrhenius expressions (derived from the rate constants of the reverse recombination reactions) was used. The temperature dependences of the high-pressure-limit rate constants of the barrierless radical recombination reactions needed in the ILT calculations were estimated based on the analysis of the existing experimental and theoretical data on cognate reactions [21–30,34–41]. The resultant parameters of the modified Arrhenius expressions are given in Table 1. The details of the analysis for individual reactions as well as those of the procedures used to calculate the k(E) dependences are presented in Supporting material. The effects of the uncertainties associated with such estimates on the rate constants and the branching fractions of the individual product channels were evaluated, as described below.

Fig. 2(a) demonstrates the energy dependences of the microcanonical rate constants of selected channels of further reaction
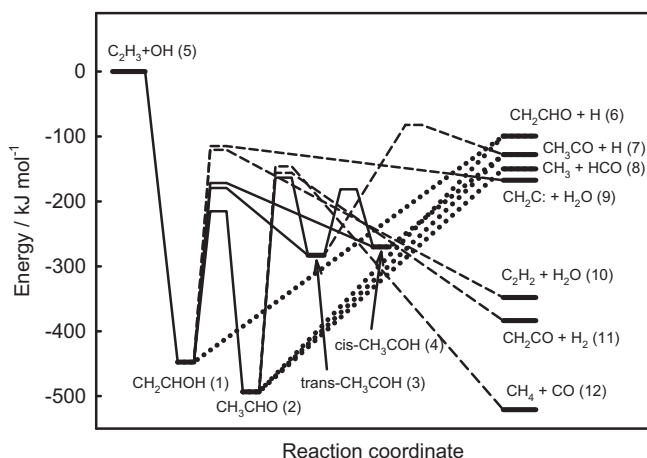

Fig. 1. Potential energy surface of reaction 1. Solid lines: addition and isomerization processes; dashed lines: decomposition into products; dotted lines: barrierless decomposition.