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OH + HONO reaction: A theoretical study

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Abstract

The reaction of OH radical with nitrous acid HONO is investigated by ab initio quantum chemistry methods. The doublet potential energy surfaces are calculated at the CCSD(T)/aug-cc-pVDZ//UMP2/6-311++G(d,p) levels. Various possible reaction pathways are considered. Among them, the most feasible pathway should be the OH radical attacking on the hydrogen of *cis*-HONO to form a 6-member-ring complex C2 barrierlessly, followed by the indirect hydrogen abstraction transition state TSabsC2-C6I to form a weakly bound complex C6, giving rise to the educts P1 $H_2O + NO_2$. Because all of the complexes, transition state, and products involved in the feasible pathway lie below the reactants, the title reaction is expected to be rapid, which in good agreement experiment. The present study may be helpful for probing the mechanisms of the HONO reactions and understanding the atmospheric chemistry.

Keywords: Reaction mechanism; Potential energy surface; OH radical; HONO

1. Introduction

Radical-molecule reactions play important roles in both combustion and interstellar processes [1]. Reactions with small or even zero barriers are of particular interest [2–6], especially in interstellar space where the temperature is low. Under these conditions, low-barrier reactions easily deplete molecules and yield new products. The reaction of hydroxyl radical with nitrous acid is very important to the chemistry of troposphere where HONO may be formed by lighting or chemical reactions in the polluted environment. Surprisingly, data on non-reactive uptake of nitrous acid on ice are scarce, given the importance of HONO for atmospheric and especially polar snow chemistry [7–10]. On the other hand, the reaction is also pivotal to our understanding of high-temperature combustion of nitrate esters, nitramines and energetic materials containing [H, N, O]-species [11]. It has been long known that nitrous acid is a key reactive intermediate during the course of chemical combustion reactions of energetic materials such as nitramines propellants [12–15]. On account of its relevancy in combustion and atmospheric chemistry, kinetic and mechanistic information on H, O, NO_2, O_3, HCl, F, HF, HNO and NH_3 initiated reaction with nitrous acid has been subject to numerous experimental and theoretical studies [16–21].

The most important chemical cleaning agent of the atmosphere is the hydroxyl radical, OH [22,23]. It determines the oxidizing power of the atmosphere, and thereby controls the removal of nearly all gaseous atmospheric pollutants [24,25]. The atmospheric supply of OH is limited, however, and could be overcome by consumption due to increasing pollution and climate change [26,27], with detrimental feedback effects. Recently Rohrer etc. reported that the concentration of OH is linear dependence on solar ultraviolet radiation [28].

Literaturely, there have been limited but conflicting kinetic data [29–38] for the OH + HONO reaction, which has been invariably assumed to occur by the abstraction reaction:

$$OH + HNO_2 \rightarrow H_2O + NO_2 \quad \Delta H = -41\ \text{kcal/mol}$$

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In the temperature range of interest to atmospheric chemistry, Cox and co-workers reported the rate constant at ambient temperature to fall within the range of $(1\text{–}4) \times 10^{-12}$ cm^3 mol^{-1} s^{-1} with small positive activation energy, 3.2 kJ/mol, and independent of pressure [30–34]. Recently, Burkholder et al. [35] determined the rate constant by LIF (laser-induced fluorescence) for OH detection and reported $k_1 = (2.8 \pm 1.3) \times 10^{-12}$ exp $[(+260 \pm 140)/\mathrm{T}]$ cm^3 mol^{-1} s^{-1} for the temperature range 298–373 K. The activation energy for the reaction was found to be −2.2 kJ/mol, clearly at odds with that of Jenkin and Cox mentioned above. Furthermore, another two conflicting rate constant expressions have been recommended: $k_1 = 3.76 \times 10^{-12}\,\mathrm{T}^{1.0}$ exp (−68/T) cm^3 mol^{-1} s^{-1} for 300–2500 K by Tsang and Herron [36] for high-temperature combustion modeling applications, $k_1 = 1.63 \times 10^{-12}$ exp (+260/T) cm^3 mol^{-1} s^{-1} at 290–380 K by Atkinson et al. [37] for atmospheric modeling applications. On the other hand, a theoretical study [11a] on the title reaction was carried out, and the equilibrium geometries and transition structures were calculated using density functional theory (DFT) method. As we know, different in geometry will lead to different reaction mechanisms and extreme care should be taken to choose an appropriate theoretical level for investigation of reactions involving radicals [39].

Thus, it is necessary to reexamine the title reaction with other theoretical method to provide theoretical knowledge accurate enough to be useful for further kinetic and thermodynamic study on radical reactions. Some conclusions that are made in this work may be helpful for further theoretical and experimental studies of this title reaction.

In the title reaction there are pre-reactive complexes.

Six pre-reactive complexes are successfully located on the doublet PESs. All the six structures with no imaginary frequencies (minima) were located at all levels of theory. As shown in Fig. 1, most of the addition and the H-abstraction reactions proceed via complexes in the title reaction. Another theoretical investigation of the isoelectronic system $C_2H_2 + O^-$ [40], shows that a collinear hydrogen-bonded complex $C_2H^- \cdots OH$ (productlike) exist on the PES, which is viewed as a direct precursor for the proton transfer. While in another isoelectronic system $C_2H_2 + OH$, there is no pre-reactive complex located on the H-abstraction path, but on the addition path [41]. On the other hand, all the ab initio calculations show that the approach of H/O atom of OH radical to HONO generates six different initial pre-reactive complexes, depending on the details of the approach geometry.

2. Computational methods

All the calculations were carried out on the SGI O3800 servers using the GAUSSIAN 98 and GAUSSIAN 03 program package [42]. Geometries of the reactants, products, intermediates and transition states (TSs) have been optimized with the unrestricted Møller–Plesset second-order perturbation UMP2 (FULL) [43] method using the 6-311G(d,p), and 6-311++G(d,p) basis sets. The presence of diffuse functions in the basis set allows for an appropriate representation of the dispersion forces that should play an important role in the stabilization of the weakly bound structures considered in this work [44]. Vibrational frequencies, also calculated at the same level of theory, have been used to characterize stationary points, zero-point energy (ZPE) corrections calculations. The number of imaginary frequencies for intermediates and transition states are 0 and 1, respectively. The ZPE and vibrational frequencies were scaled by a factor of 0.95 for anharmonicity correction [45]. To confirm that the transition states connect between designated intermediates, intrinsic reaction coordinate (IRC) [46] calculations were performed at the UMP2/6-311++G(d,p) level of theory.

For the purpose of obtaining more reliable energies of various structures, the coupled-cluster CCSD(T) method with Dunning's correlation-consistent augmented aug-cc-pVDZ basis set [47,48] was used. The UMP2/6-311++G(d,p) optimized geometries were used for the single-point coupled cluster calculations without reoptimization at the CCSD(T)/aug-cc-pVDZ.

The major problem in the application of unrestricted single determinant reference wave function is that of contamination with higher spin states. The severe spin contamination could lead to a deteriorated estimation of the barrier height [49,50]. We have examined the spin contamination before and after annihilation for the radical species and transition states involved in the OH + HONO reaction. For doublet systems, the expectation values of $\langle S^2 \rangle$ after annihilation range from 0.75 to 0.80 (the exact value for a pure doublet is 0.75) except for one complex and six unimportant transition states on the potential energy surface (0.80–0.87). This suggests that the wave function is not severely contaminated by states of higher multiplicity [51,52].Therefore, we expect that the CCSD(T)//MP2 calculations reported in this work are, in this regard, reliable.

The thermodynamic functions (ΔH and ΔG) are estimated within the ideal gas, rigid-rotor, and harmonic oscillator approximations. A temperature of 298.15 K and a pressure of 1 atm were assumed.

3. Results and discussion

For the present H_2NO_3 system, there are enantiomorphs. For convenient and clear discussion, we only present moieties of reaction channels that have enantiomorphic varieties and some important nantiomorphous structures. The structures of the reactants, complexes, intermediate isomers, transition states and products are depicted in Fig. 1. By means of the interrelation among the reactants, isomers, transition states, and products as well as the corresponding relative energies, the schematic profiles of the doublet potential energy surfaces are depicted as shown in Figs. 2, 3 and Fig. S3. The calculated