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Ozonization of C_{70} and subsequent thermolysis of ozonide 1,2-$C_{70}O_3$: A theoretical study

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ABSTRACT

Semiempirical method AM1 was employed to investigate the ozonization of [70]fullerene (C_{70}) and the following extrusion of molecular oxygen from ozonide 1,2-$C_{70}O_3$. Our computational results show that (i) among the eight different bonds of C_{70} that may react with ozone, the C1—C2 and C5—C6 bonds are the two most active pair sites with near the same energy barriers; (ii) there are six different pathways to extrude molecular oxygen from ozonide 1,2-$C_{70}O_3$, of which one results in 1,6-oxidoannulene, one affords 2,3-oxidoannulene, the other four lead to 1,2-epoxide. It is most likely that the formation of 1,2-epoxide proceeds via two parallel routes with similarly lower-energy profiles, which are favored both thermodynamically and kinetically. Several new intermediates and transition states have been located for the thermolysis of ozonide 1,2-$C_{70}O_3$ to epoxide 1,2-$C_{70}O$. Four steps are required for the seemly simple conversion of 1,2-$C_{70}O_3$ to 1,2-$C_{70}O$.

1. Introduction

Fullerene oxides are useful precursors for further functionalizations [1,2]. Many efforts have been devoted to synthesize fullerene oxides by photooxygenation [3,4], electrochemical oxidation [5], ozonization [6–8], etc. The unstable [6,6]-closed ozonide intermediate $C_{60}O_3$, which could be isolated from the reaction mixture of C_{60} and ozone, decomposed rapidly to [6,6]-closed epoxide $C_{60}O$ at ambient temperature [9]. The ozonization of C_{60} and the dissociation of the formed ozonide $C_{60}O_3$ have been investigated theoretically at the AM1 level [10]. However, as for C_{70}, the second most abundant fullerene, reactions are much more complex due to its eight different bonds, i.e., C1—C2, C5—C6, C7—C8, C7—C21, C2—C3, C1—C6, C6—C7, and C20—C21 bonds, as shown in Chart 1. After the isolation of the oxide $C_{70}O$ from fullerene soot in 1991 by Diederich et al. [11], many procedures for the preparation of C_{70} oxides and ozonides have been reported [12–16]. In 2001, Heymann et al., presented their complete study of ozonization of C_{70} and the subsequent photolysis and thermolysis of the formed ozonides [17]. 1,2- and 5,6-ozonides $C_{70}O_3$ could be obtained and isolated when a stream of ozone was slowly bubbled into chilled solution of C_{70}. The 1,2-ozonide thermally dissociated to 1,2-epoxide. Surprisingly, the 5,6-ozonide decayed to 7,8-oxidoannulene. Upon photolysis, the 1,2-ozonide gave 2,3-oxidoannulene exclusively, while the 5,6-ozonide generated a mixture of 1,6-oxidoannulene, 6,7-oxidoannulene and 5,6-epoxide.

Wang's group [18] and Zhao's group [19] have studied the ozonolysis of C_{70} theoretically by means of the AM1 method. Even though Wang et al. calculated the heats of formation of ozonides $C_{70}O_3$ and oxides $C_{70}O$, they did not provide the energy barriers for the ozonization and thermolysis reactions [18]. Zhao and coworkers explored the ozonization of C_{70} only at C1—C2 and C20—C21 bonds, and considered only one pathway for the subsequent O_2 elimination [19]. In continuation of our interest in theoretical study on fullerene chemistry [20] and in order to better understand why 1,2- and 5,6-ozonides $C_{70}O_3$ were favorably formed, and why only 1,2-$C_{70}O$ isomer from the thermolysis of 1,2-$C_{70}O_3$ was obtained experimentally, herein we present the systematic studies on all eight possible routes for the ozonization of C_{70} and six possible pathways for the subsequent O_2 extrusion from ozonide 1,2-$C_{70}O_3$ at the semiempirical AM1 level.

2. Method of calculation

The AM1 [21–27] semiempirical method is one of the most popular methods used for the theoretical studies of big molecular systems. The large size of the fullerene cage prevents the use of DFT and ab initio molecular quantum mechanical methods to perform optimization. Therefore, all calculations in this work were

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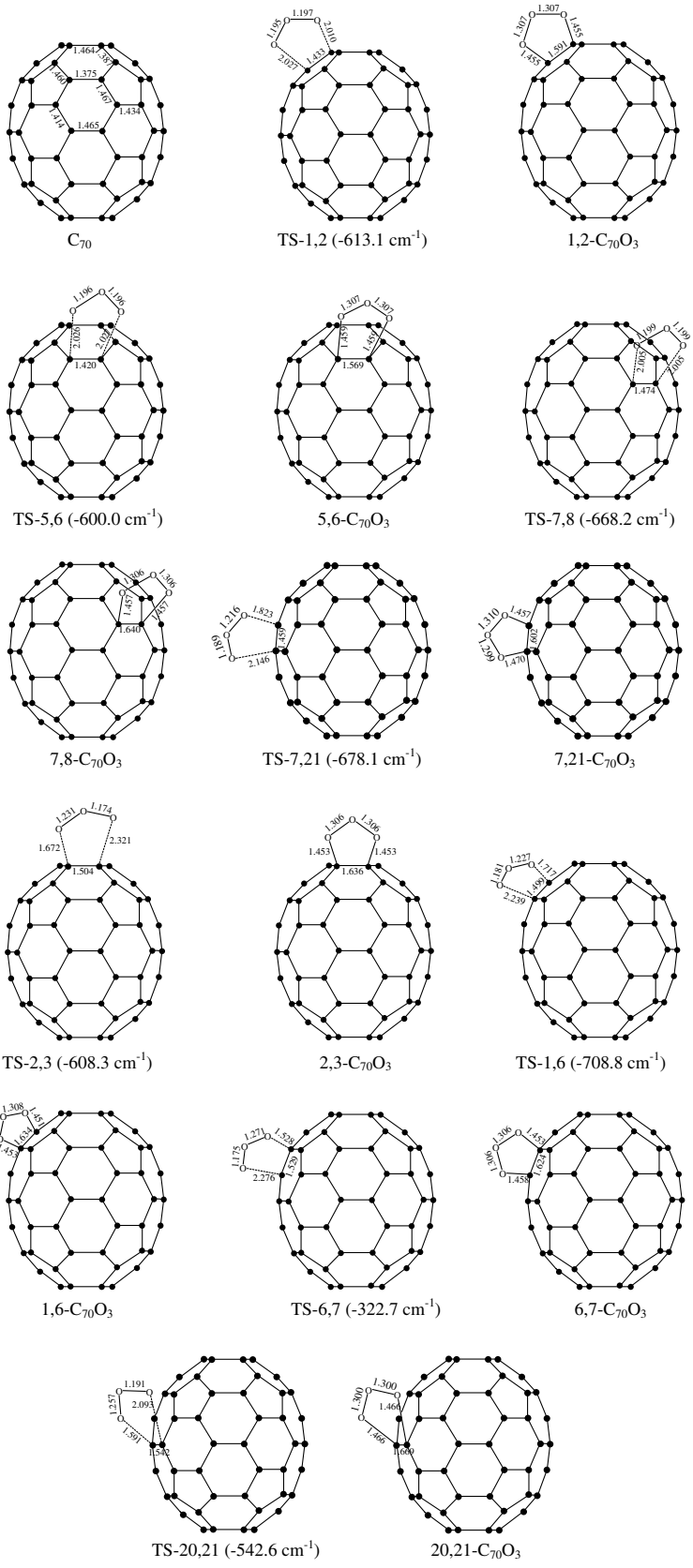

Fig. 1. Key parameters of the AM1-optimized geometries of transition states and ozonides for the reaction of ozone with C_{70}. The unit of bond length is in Å (10^{-9} m). Those in parenthesis are imaginary frequencies of the transition states, and the dashed lines refer to the corresponding vibrational modes.