C_{70} oxides and ozonides and the mechanism of ozonolysis on the fullerene surface. A theoretical study.

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Streszczenie

A series of ab initio calculations have been carried out to determine why the *a*,*b*- and *c*,*c*-isomers are the most commonly observed mono-oxides of C_{70} in ozonolysis reactions, when existing calculations in the literature report that these structures are not the most stable conformations. We show that the *a*,*b*- and *c*,*c*-isomers are the two most stable structures on the $C_{70}O_3$ potential energy surface, which suggests that the reaction pathway toward oxide formation must proceed via the corresponding ozonide structure. From our calculations, we offer a mechanism for the thermally induced dissociation of $C_{70}O_3$ that share the first two steps with the general mechanism for ozonolysis of alkenes proposed by Criegee. We suggest further steps that involve $C_{70}O_3$ losing O_2 in its triplet or singlet state, thus leaving $C_{70}O$ in its triplet or singlet state, respectively. A pair of products in their singlet states seems to be more likely for the decomposition of *a*,*b*-$C_{70}O_3$, which ultimately leads to the closed *a*,*b*-$C_{70}O$ epoxide structure. For *c*,*c*-$C_{70}O_3$, the more thermodynamically favorable route is the triplet channel, resulting in the triplet open *c*,*c*-$C_{70}O$ oxidoannulene structure, which may subsequently decay to the singlet ground state *c*,*c*-$C_{70}O$ epoxide form. This finding offers an alternative interpretation of the experimental observations which reported an open *d*,*d*-$C_{70}O$ oxidoannulene structure as the metastable intermediate.

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https://www.acs.org/content/acs/en.html