Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Roaming as the Dominant Mechanism for Molecular Products in Photodissociation of Large Aliphatic Aldehydes

Po-Yu Tsai,[1] Hou-Kuan Li,[2] Toshio Kasai,[2,3] and King-Chuen Lin[2,*]

1. **Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan**
2. **Department of Chemistry, National Taiwan University, Taipei 106, and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan**
3. **Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan**

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A. Tight and Roaming saddle points of 2,2-dimethyl propanal

The tight and roaming SPs of 2,2-dimethyl propanal ($CH_3C(CH_3)_2CHO$) are found by using B3LYP /6-311++G(d,p) and CASSCF(6e,6o)/6-311++G(d,p), respectively. The geometries are shown in Fig.1S. The active space of CASSCF calculation includes π/π* of CO, σ/σ* of OC-H and HCO---C_4H_9. The energy difference between asymptotic radical and roaming SP is calculated at (6e,6o)-MRMP2/6-311++G(d,p) level with the same active space. The HCO and C_4H_9 radical fragments are optimized independently via CASSCF(7e,7o)/ 6-311++G(d,p) and CASSCF(3e,3o)/6-311++G(d,p), respectively. The asymptotic MRMP2 energies of the radicals are computed by using the CASSCF optimized radical geometries with the two fragments far separated from each other (~100 Å). The MRMP2/6-311++G(d,p) result (including zero-point energy from CASSCF calculation) shows that the roaming SP is 3 kJ/mol below the asymptotic limit of radical channel.

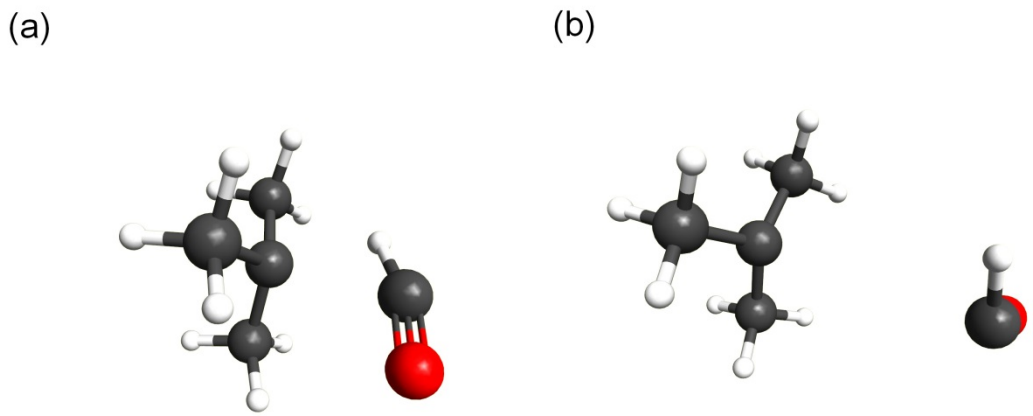

Fig.1S The geometries of 2,2-dimethyl propanal. (a)tight SP and (b) roaming SP optimized by B3LYPand CASSCF methods, respectively.