Autor(en) des Beitrags:
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Titel des Beitrags:
Quantitative Representation of Specific Rate Constants k(E) for the Photoisomerization of Diphenylpolyenes: The Solution of a Longstanding Problem

Abstract:
Specific rate consts. k(E) of the photoisomerization of four isotopomers of trans-stilbene, of 4-chloro-(4CS) and 4-methyl-trans-stilbene (4MS), of all-trans-1,4-diphenyl-1,3-butadiene (DPB), and of 4-(dimethylamino)-4'-cyanostilbene (DCS) are represented by conventional RRKM theory, using new ab initio calcns. of excited state frequencies. Data from supersonic beam expts. are reproduced quant. when the barrier heights are fitted to the expts. and activated complex frequencies are taken unchanged from the parent mols. The main difference to earlier work lies in the smaller frequencies now calc'd. for the reaction coordinates. The results of this work clearly support an adiabatic mechanism of the reaction which can very well be quantified by statistical unimol. rate theory. [on SciFinder(R)]

Stichworte:
Density functional theory (B3LYP quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) CI (CIS quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Transition state theory (RRKM quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Excited singlet state (S1 quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Isotope effect (deuterium quant. representation of specific rate consts. k(E) for
photoisomerization of diphenylpolyenes) Polyenes Role: CPS (Chemical process), PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), RACT (Reactant or reagent) (diphenylpolyenes quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Vibrational frequency (excited state and reaction coordinate quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Isomerization (photoisomerization, adiabatic cis-trans quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Isomerization kinetics (photoisomerization, cis-trans quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) AM1 Ab initio methods Activation energy Basis sets Normal modes Potential barrier Transition state structure Zero point energy (quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) Isotopomers Role: CPS (Chemical process), PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), RACT (Reactant or reagent) (quant. representation of specific rate consts. k(E) for photoisomerization of diphen Potential energy hypersurface (reaction coordinate quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes) quant representation specific rate const photoisomerization diphenylpolyene

Kongresstitel:
CAN 137:62959 22-6 Physical Organic Chemistry Institut fuer Physikalische Chemie, Universitaet Goettingen, Goettingen, Germany. Journal 1089-5639 7782-39-0 (Deuterium) Role: CPS (Chemical process), PEP (Physical, engineering or chemical process), PRP (Properties), PYP (Physical process), PROC (Process) (isotope effect; quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes); 103-30-0; 538-81-8; 1657-50-7; 1860-17-9; 2844-17-9; 5284-44-6; 16341-52-9; 20748-24-7 Role: CPS (Chemical process), PEP (Physical, engineering or chemical process), PRP (Properties), RCT (Reactant), PROC (Process), RACT (Reactant or reagent) (quant. representation of specific rate consts. k(E) for photoisomerization of diphenylpolyenes)

Zeitschriftentitel:
J. Phys. Chem. A

Jahr:
2002

Band:
106

Heft / Issue:
22

Seiten:
5510-5516

Occurences:
Einrichtungen > Fakultäten > Fakultät für Chemie > Department Chemie > Lehrstuhl für Physikalische Chemie (Prof. Heiz) > old_publications [1342767] > misc_until_2003 > 2002

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