

1,3-Sigmatropic shifts in carbonylketenes, carbonyl isocyanates and analogous compounds

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Abstract: Antarafacial 1,3-sigmatropic shifts in carbonyl derivatives of ketenes, isocyanates, thioketenes and thioisocyanates have been studied by means of ab initio MO calculations. Energy barriers in 20 different systems have been uniformly determined at the MP4SDTQ/6-31G(d,p) level, based on MP2/6-31G(d,p) geometries and corrected for zero-point energies. For formylketene, higher-level calculations using the QCISD(T) method and larger basis sets [up to 6-311++G(2df,2p)] have also been carried out. In carbonylketenes, the migratory aptitude of the substituents R is established as follows: $\text{Cl} > \text{SH} > \text{NF}_2 > \text{NH}_2 > \text{BH}_2 > \text{PH}_2 > \text{F} > \text{OCH}_3 > \text{OH} > \text{SiH}_3 > \text{H} > \text{C}_6\text{H}_5 > \text{CH}_3$. The barrier heights range from 10 kcal/mol for Cl migration to 35 kcal/mol for phenyl migration. Several factors influencing the energy barriers including the existence of an n-electron pair at the migrating atom, its size, electronegativity and ability to adapt to a hypervalent state, as well as the strengths of the breaking and forming bonds have been examined in detail. Generally speaking, 1,3-sigmatropic rearrangements are feasible thermal unimolecular reactions even under mild experimental conditions.

Author Keywords: 1,3-Sigmatropic shifts; Ab initio MO calculations; Carbonyl isocyanates; Carbonylketenes; Ketenimines; Thioisocyanates; Thioketenes

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