RAPID ALLYLIC 1,6 H-ATOM TRANSFER IN A CRIEGEE INTERMEDIATE WITH UNSATURATED SUBSTITUENTS

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A new allylic 1,6 H-atom transfer mechanism is established through infrared (IR) excitation of the 2-butenal-oxide Criegee intermediate [CH_3CH=$CHCHOO$]. Rapid 1,6 H-atom transfer is facilitated for certain conformers of 2-butenal oxide by extended conjugation across the vinyl and carbonyl oxide groups. A low-energy conformer (*tZZ*) of 2-butenal oxide is identified by IR action spectroscopy in the fundamental CH region with ultraviolet (UV) detection of OH products by laser-induced fluorescence (LIF). The strongest observed IR transition at 2996 $\mathrm{cm}^{-1}$is consistent with the anharmonic frequency computed for the *tZZ* conformer. A low energy reaction pathway involving isomerization of 2-butenal oxide from a lower energy conformer (*tZZ*) to a higher energy conformer (*cZZ*), followed by 1,6 H-atom transfer via a 7-membered ring transition state with relatively low ring strain, is theoretically predicted and shown experimentally to yield the OH products. The rapid appearance of OH products (ca. $2.3 \pm 1.0 \times 10^8$ s^{-1}) agrees with a statistical RRKM calculation for an effective reaction rate (k_{eff}(E) on the order of 10^8 s^{-1} at ca. 3000 cm^{-1}) including tunneling. Unimolecular decay involves a combination of conformational isomerization and unimolecular dissociation via 1,6 H-atom transfer. The excellent agreement between experiment and theory confirms the allylic 1,6 H-atom transfer mechanism in 2-butenal-oxide Criegee intermediate and provides a novel pathway for non-photolytic OH generation upon alkene ozonolysis in the troposphere.