

FORMATION REACTION MECHANISM AND INFRARED SPECTRA OF CRIEGEE INTERMEDIATE ANTI-TRANS-METHACROLEIN OXIDE [CH₂C(CH₃)CHOO] AND ITS ASSOCIATED PRECURSOR AND ADDUCT RADICALS

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Methacrolein oxide (MACRO, CH₂C(CH₃)CHOO) is an important Criegee intermediate produced in ozonolysis of isoprene, the most abundantly-emitted non-methane hydrocarbon in the atmosphere. We employed a step-scan Fourier-transform infrared spectrometer to investigate the source reaction of MACRO in laboratories. Upon UV irradiation of precursor 1,3-diiodo-2-methyl-prop-1-ene CH₂IC(CH₃)CHI (**1**), the 3-iodo-2-methyl-prop-1-en-3-yl CH₂C(CH₃)CHI radical (**2**) was detected, confirming the fission of the allylic C-I bond rather than the vinylic C-I bond. Upon UV irradiation of (**1**) and O₂ near 21 Torr, *anti-trans*-MACRO (**3a**) was observed to have an intense OO-stretching band near 917 cm⁻¹, much greater than those of *syn*-CH₃CHOO and (CH₃)₂COO, supporting a stronger O-O bond in MACRO because of resonance stabilization. At increased pressure (86-346 Torr), both reaction adducts CH₂C(CH₃)CHIOO (**4**) and (CHI)C(CH₃)CH₂OO (**5**) radicals were observed, indicating that O₂ can add to either carbon of the delocalized propenyl radical moiety of (**2**). We also employed a quantum-cascade laser and an UV laser to investigate the yield and kinetics of MACRO. The yield of MACRO is only 5 % from the source reaction, significantly smaller than other carbonyl oxides. The rate coefficients of the formation reaction and the self-reaction of MACRO will also be discussed.