

The OH-initiated oxidation of CS₂ in the presence of NO : FTIR matrix-isolation and theoretical studies.

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Streszczenie

We studied the photochemistry of the carbon disulfide–nitrous acid system with the help of Fourier transform infrared (FTIR) matrix isolation spectroscopy and theoretical methods. The irradiation of the CS₂⋯HONO complexes, isolated in solid argon, with the filtered output of the mercury lamp ($\lambda > 345$ nm) was found to produce OCS, SO₂, and HNCS; HSCN was also tentatively identified. The ¹³C, ¹⁵N, and ²H isotopic shifts as well as literature data were used for product identifications. The evolution of the measured FTIR spectra with irradiation time and the changes in the spectra after matrix annealing indicated that the identified molecules are the products of different reaction channels: OCS being a product of another reaction path than SO₂ and HNCS or HSCN. The possible reaction channels between SC(OH)S/SCS(OH) radicals and NO were studied using DFT/B3LYP/aug-cc-pVTZ method. The SC(OH)S and/or SCS(OH) intermediates are formed when HONO attached to CS₂ photodissociates into OH and NO. The calculations indicated that SC(OH)S radical can form with NO two stable adducts. The more stable SC(OH)S⋯NO structure is a reactant for a simple one-step process leading to OCS and HONS molecules. An alternative, less-stable complex formed between SC(OH)S and NO leads to formation of OCS and HSNO. The calculations predict only one stable complex between SCS(OH) radical and NO, which can dissociate along two channels leading to HNCS and SO₂ or HSCN and SO₂ as the end products. The identified photoproducts indicate that both SC(OH)S and SCS(OH) adducts are intermediates in the CS₂ + OH + NO reaction leading to different reaction products.

Adres publiczny

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