Structural and FTIR spectroscopic studies of matrix-isolated 3-thio-1,2,4-triazole complexes with carbon dioxide. The UV-induced formation of thiol···CO_2 complexes

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Streszczenie

Matrix isolation FTIR spectroscopy was combined with quantum chemical calculations to characterize complexes of 3-thio-1,2,4-triazole (ST) with carbon dioxide. Geometries of the possible 1 : 1 and 1 : 2 complexes were optimized at the DFT (B3LYPD3) level of theory with the 6-311++G(3df,3pd) basis set. The computational results show that ST interacts specifically with carbon dioxide through different hydrogen bond and van der Waals interactions. For the 1 : 1 complexes of the most abundant ST thione tautomer, four stable minima, ST*n*···CO_2, have been located on the potential energy surface. In contrast, for the ST thiol tautomer, three STl···CO_2 structures were optimized. Experimentally, the two most stable 1 : 1 complexes of ST*n* with CO_2, characterized by the presence of the N–H···O hydrogen bridge and an additional S6···C10 interaction, were identified in solid argon upon deposition. Annealing of the matrix at 32 K proved that one 1 : 2 structure is also present, resulting from the addition of a second CO_2 molecule to the 1 : 1 complexes. The laser irradiation at λ = 270 nm, apart from generating the thiol tautomer of ST, also leads to the formation of three thiol···CO_2 complexes. Furthermore, the presence of CO_2 in the argon matrix was found to influence the efficiency of the UV-induced thione–thiol tautomerization, though to a lesser extent than nitrogen. This suggests that while CO_2 forms stronger intermolecular interactions with ST, its impact on tautomerization kinetics is less pronounced, highlighting the nuanced role of specific gas-phase interactions in modulating photochemical transformations in low-temperature matrices. The findings presented in this work not only enhance the fundamental understanding of weak intermolecular interactions but also provide new insights into the role of CO_2-specific effects in photochemical and structural transformations of heterocycles.

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