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Pyrrolecarbodithioates Formation: a Theoretical Study

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The recent studies of pyrrole anions addition to carbon disulfide in KOH-DMSO superbase system have shown that the reaction direction depends on pyrrole ring substitution: an unsubstituted pyrrole selectively forms pyrrole-1-carbodithioate, whereas 2-methyl-, 2,3- and 2,4-dimethylpyrroles give exclusively pyrrole-2-carbodithioates under the same conditions, and 2,5-dimethylpyrrole reaction results in only 2,5-dimethylpyrrole-3-carbodithioate. The reaction of 2-phenylpyrrole with CS_2 yields the 1:2 ratio of 2-phenyl-1- and 5-carbodithioates.

The pyrrole, mono- and dimethylsubstituted pyrrole, and 2-phenylpyrrole anions addition to carbon disulfide was studied using ab initio RHF/6-31+G* and MP2/6-31+G* approaches as well as the density functional theory (B3LYP/6-31+G*).

The pyrrole-2-carbodithioates were found to be the most stable for both unsubstituted pyrrole and its derivatives. The 1-adduct is 5.3 kcal/mol less favorable in pyrrole, and the same energy difference remains in 2-phenylpyrrole adducts. On the contrary, the energy gap between 2-methylpyrrole-5-carbodithioate and 2-methylpyrrole-1-carbodithioate increases up to 11.3 kcal/mol due to the steric hindrances. The same effect in 2,5-dimethylpyrrole makes the 2,5-dimethylpyrrole-1-carbodithioate substantially unfavorable even compared to the 2,5-dimethylpyrrole-3-carbodithioate.

Two different pathways were considered for a pyrrole anion addition to carbon disulfide with 2-position. Both mechanisms suppose the σ-complex formation. In the latter this complex may be rearranged towards pyrrole-2-carbodithioate *via* direct 1,2-hydrogen shift or via consequent stages including intermediate S-H bond formation. The limiting stages of both mechanisms are associated with comparable activation barriers 16.8 kcal/mol. No activation barrier was found on the pyrrole-1- carbodithioate formation pathway, and this can cause a kinetic formation of less stable isomer. By contrast, a significant activation barrier appeared in 2-methylpyrrole addition to CS_2, and the reaction yields the most stable 2-methylpyrrole-5-carbodithioate. The intermediate value occurred for 2-phenylpyrrole anion addition to CS_2 with 1-position. Along with a reduced binding energy in 2-phenylpyrrole-1- and 5-carbodithioates compared to those in the adducts of pyrrole and its methylsubstituted anions it causes both 1- and 5- adducts formation.

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