UNUSUAL SECONDARY KINETIC ISOTOPE EFFECTS IN REACTION OF TERTIARY PHOSPHINES WITH ELECTRON-DEFICIENT ALKENES

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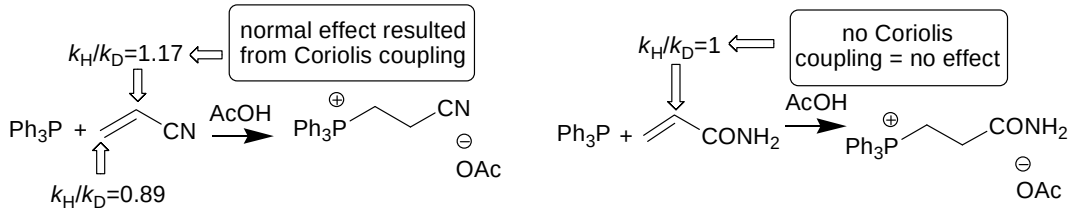
Secondary kinetic isotope effects (KIEs) were determined for the reaction of PPh_3 with 2-*d*-acrylonitrile, d_3-acrylonitrile, and 2-*d*-acrylamide in acetic acid solution [1,2].



In the reaction of acrylonitrile, the replacement of H by D on the position β to the CN group expectedly produced inverse secondary KIE (k_H/k_D=0.89±0.01). However, the isotope labeling at the α-position of acrylonitrile surprisingly led to normal secondary KIEs (k_H/k_D=1.17±0.02). These normal effects were interpreted in terms of known vibrational-rotational (Coriolis) coupling between the out-of-plane and the in-plane C–C≡N bending modes resulted from rapid rotation of acrylonitrile molecule with an angular velocity strongly dependent on the H/D substitution [3]. By the influence of the Coriolis force, the out-of-plane bending in the isotopomeric acrylonitriles contributes differently to the in-plane bending, which defines the reaction coordinate during rehybridization of nitrogen atom from sp in the CN group to sp^2 in enimine moiety (C=C=NH) at the rate-determining protonation of phosphonium zwitterionic intermediate by acetic acid. The observation of normal secondary KIEs became possible due to dynamic behavior of the intermediate zwitterion, whose very high potential energy allows to convey the history of its formation on the second reaction step of proton transfer. Calculated lifetime of the zwitterionic intermediate was only 138 femtoseconds. The untypical origin of secondary KIEs related to the α-position of acrylonitrile was evidenced by the absence of such effect for the reaction of 2-*d*-acrylamide (k_H/k_D=1.01±0.02).

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[1] A.V. Salin, ChemistrySelect 2017, 2, 6984.

[2] A.V. Salin, R.Z. Musin, J. Labelled Compd. Radiopharm. 2018, 61, 595.

[3] Z. Kisiel, L. Pszczółkowski, B.J. Drouin, C.S. Baruer, S. Yu, J.C. Pearson, J. Mol. Spectrosc. 2009, 258, 26.