

Negative Apparent Activation Energies, V-Shaped Temperature Dependences, and Pressure Dependence of “Simple Metathesis Reactions” with “Negative Barriers”

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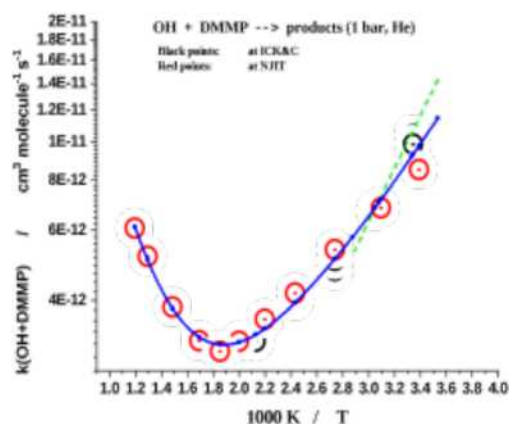
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Elementary chemical reactions that exhibit “negative apparent activation energies” (i.e., the reactions that slow down with temperature) are discussed. Discovered early negative apparent activation energies in the reactions of small hydrocarbon free radicals with hydrogen halides ($R + HX$, $R=CH_3$, C_2H_5 , C_3H_7 , etc., $X = I, Br, Cl$) stirred momentous controversy in the kinetics and thermodynamics’ community in view of the importance as an individual issue of fundamental chemical kinetics, and particularly, due to the tremendous impact on the determination of the C-H bond strengths in hydrocarbons.¹

These observations were explained based on the concept of reactions having a “negative” or “submerged” barrier, i.e., reactions having “transition states” with the ground state lying below the ground state of the reactants.² Beyond explaining the negative temperature dependences of such reactions, the theory also predicts the V-shaped temperature dependences and bath gas pressure dependences at high pressures.

Recently, we discovered a new class of reactions, which exhibit all features predicted for the reactions with negative barriers.³ These are reactions of hydroxyl radicals with organophosphorus compounds. Three such reactions were experimentally studied, reactions of OH with trimethyl phosphate (TMP), dimethyl methyl phosphonate (DMMP), and trimethyl phosphite (TMPi). In all cases, V-shaped temperature dependences were observed (negative at low and positive at elevated temperatures). An example (reaction OH + DMMP) is shown in the figure. For this reaction, the bath gas pressure dependence was also observed (1 – 30 bar, He).



[1] D. Gutman, *Acc. Chem. Res.* **1990**, *23* (11), pp. 375–380.

[2] L.N. Krasnoperov et al., *J. Phys. Chem. A* **2006**, *110*(9), pp. 3110–3120.

[3] X. Zhang et al. *Molecules*, **2022**, *27*(7), 2301; *RSC Advances*, **2021**, *11*(23), 14121-

14131.