Ab initio study of in-situ Nitroxide Mediated Polymerization: level of theory study and assessment of nitrone structure influences on thermodynamics and kinetics

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IDECAT — Integrated Design of Catalytic Nanomaterials for a Sustainable Production

Principle of Nitroxide Mediated Polymerization

nitroxide — active species

alkoxyamine — dormant polymer

+M (monomer)

In-situ formed from precursors:
- Nitrones
- Nitroso compounds

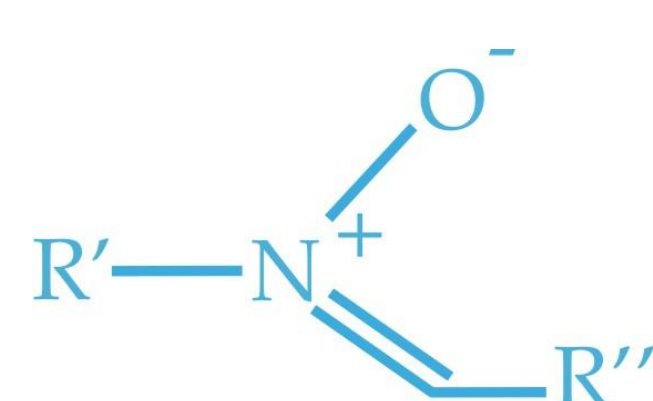$R''' — N = O$

Objectives NMP:
- Polydispersity index close to unity
- Linear growth polymer as a function of monomer conversion
- End group functionality

Objectives:
- Selection of a cost-efficient method to study compounds and reactions involved in in-situ NMP
- Description of reactions related to in-situ NMP with the selected method capturing the difference in reactivity of the precursor nitrones
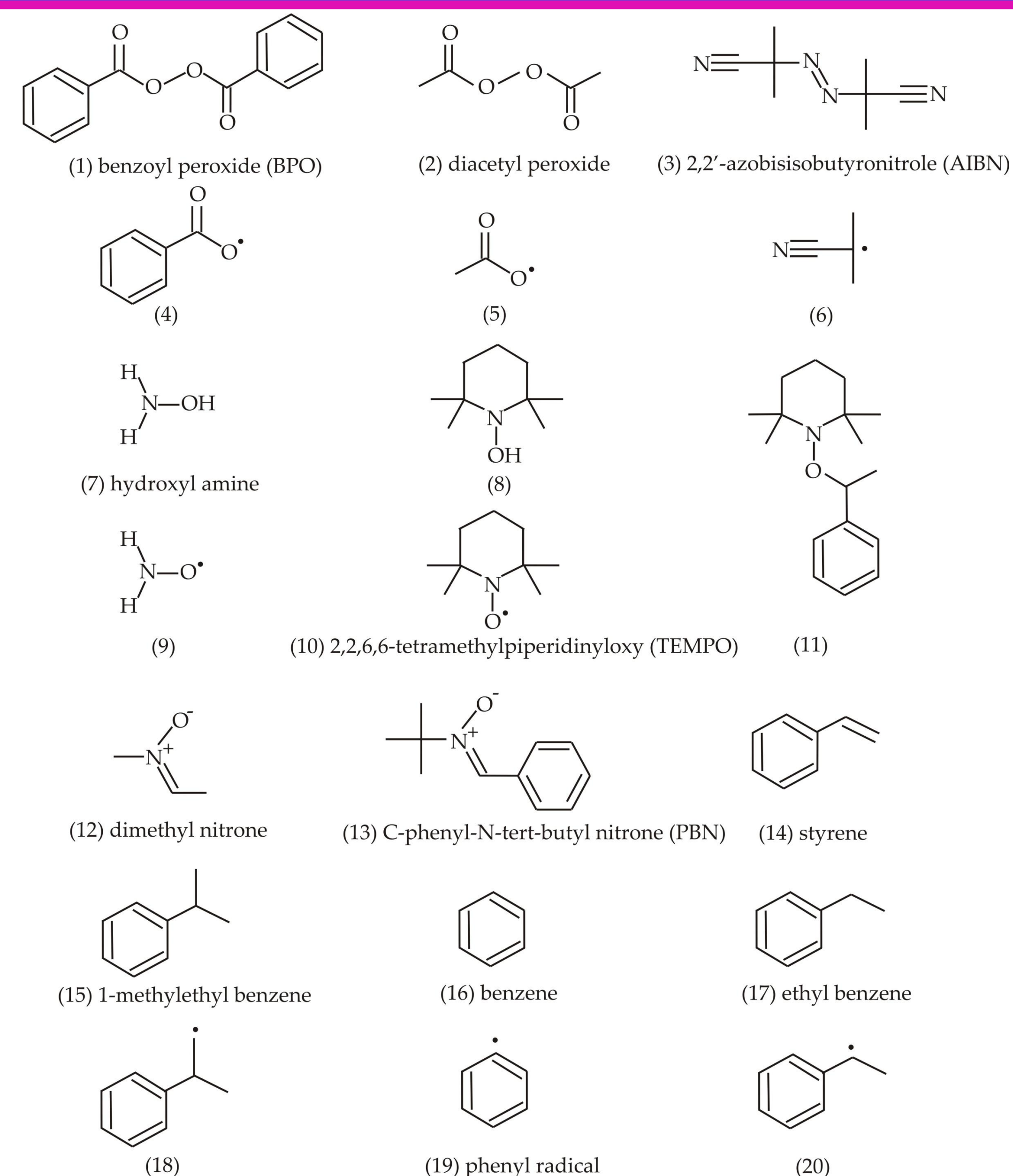
Level of theory study: test set

(1) benzoyl peroxide (BPO)
(2) diacetyl peroxide
(3) 2,2'-azobisisobutyronitrile (AIBN)
(4)
(5)
(6)
(7) hydroxyl amine
(8)
(9)
(10) 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)
(11)
(12) dimethyl nitrone
(13) C-phenyl-N-tert-butyl nitrone (PBN)
(14) styrene
(15) 1-methylethyl benzene
(16) benzene
(17) ethyl benzene
(18)
(19) phenyl radical
(20)
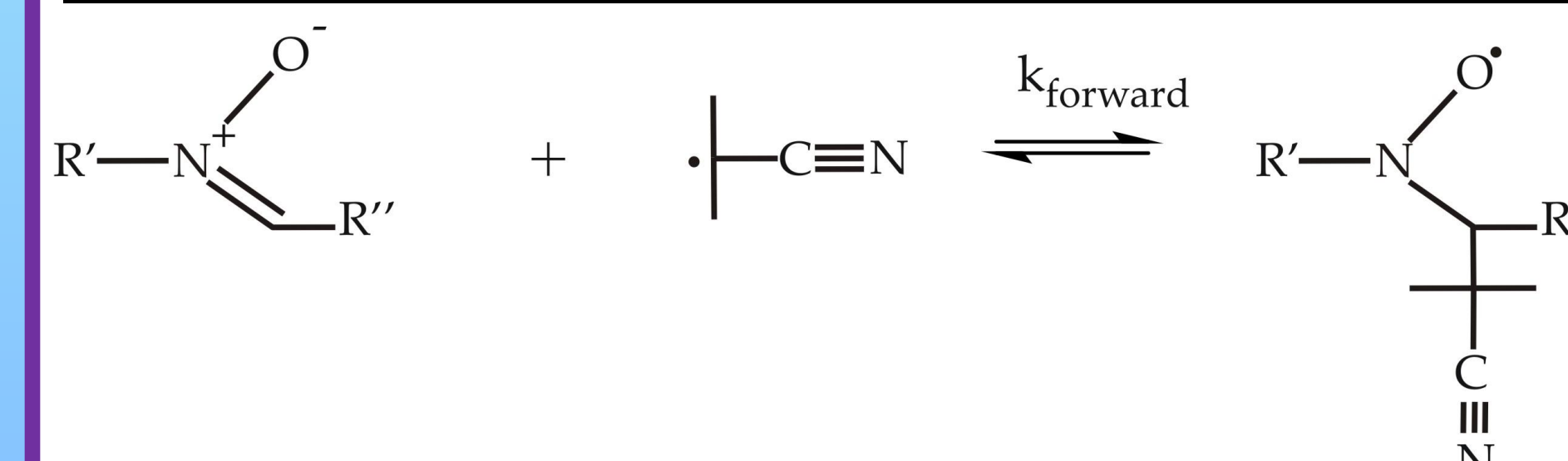
Application: nitroxide- and alkoxyamine-forming reactions

Application of the most appropriate level of theory to the calculation of nitroxide- and alkoxyamine-forming reactions of a typical system comprising 2,2'-azobisisobutyronitrile (AIBN), styrene and a nitrone.
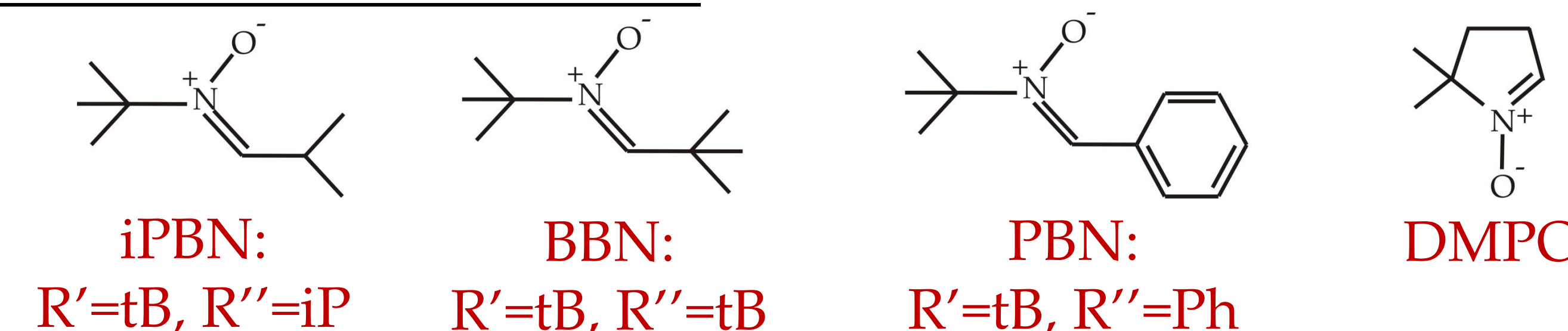
Formation of nitroxides: addition of initiating radical to nitrone:

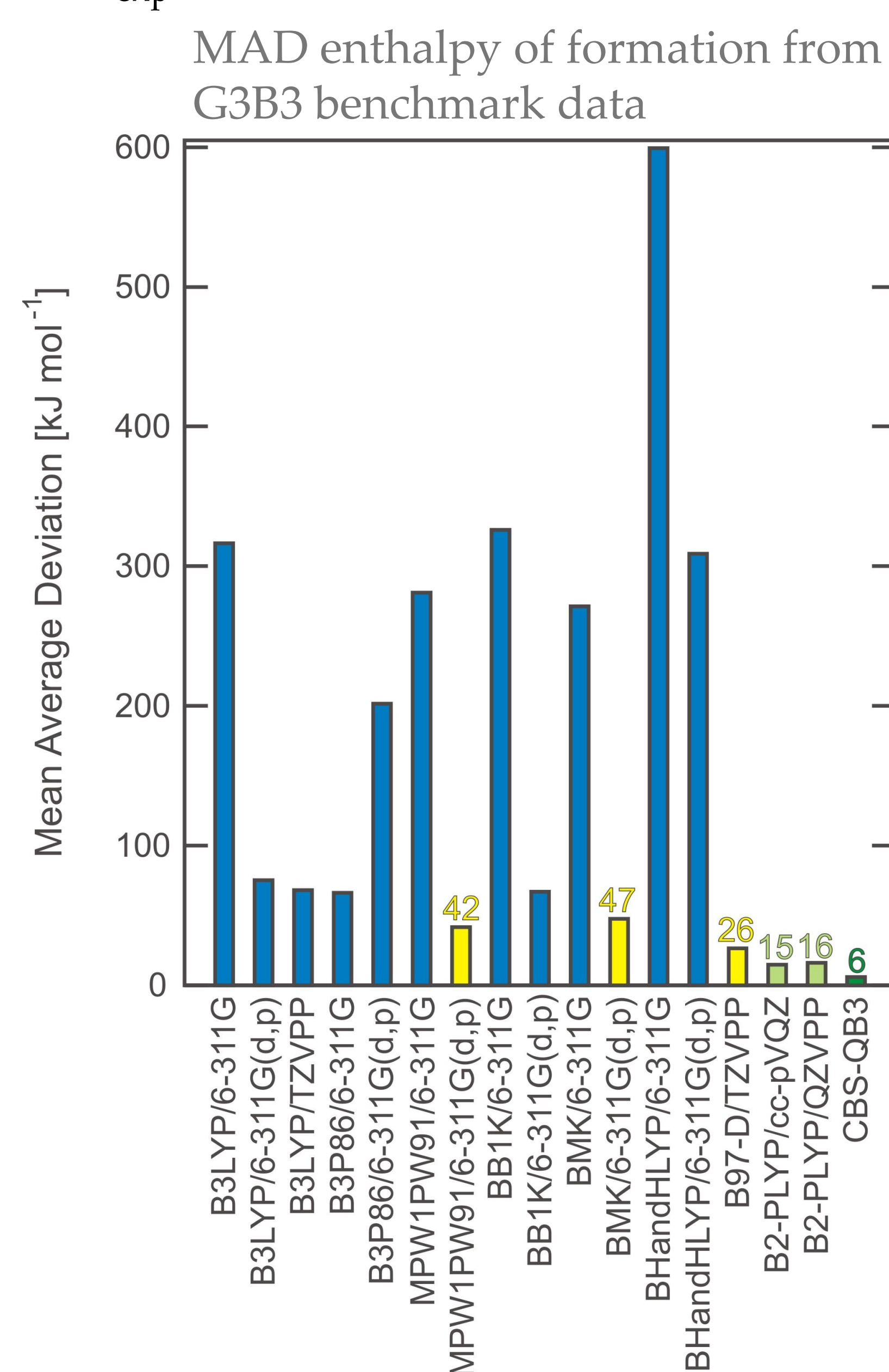**Formation of alkoxyamines (in-situ): recombination of nitroxide with radical:**

Variation of nitrone structure:

iPBN: R'=tB, R''=iP
BBN: R'=tB, R''=tB
PBN: R'=tB, R''=Ph
DMPO
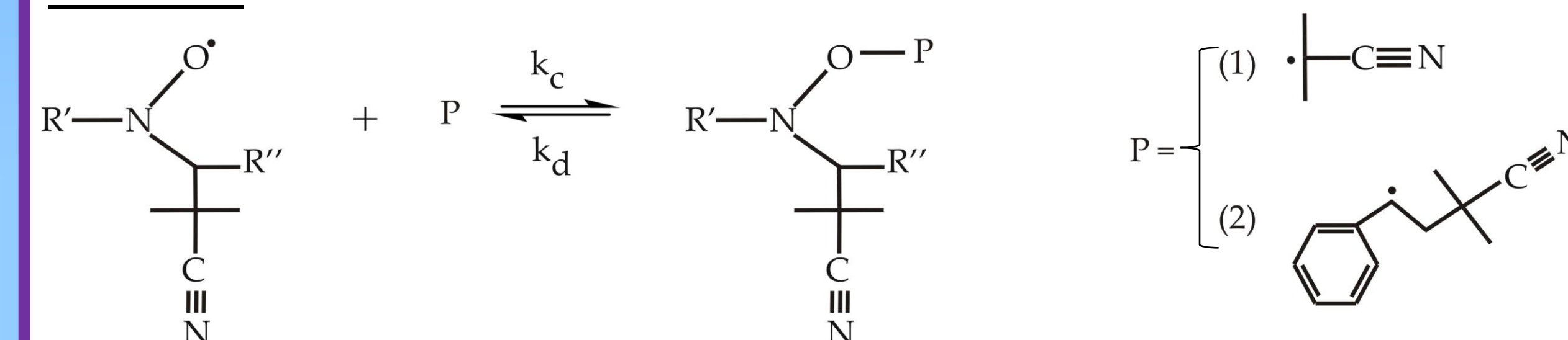
Level of theory study: results

Standard enthalpies of formation:

$MAD_{exp}(G3B3) = 4.2$ kJ mol^{-1}

MAD enthalpy of formation from G3B3 benchmark data

Mean Average Deviation [kJ mol^{-1}]

(bar labels: 42, 47, 26, 15, 16, 6)

Best-performing DFT method: B2-PLYP/cc-pVQZ

Scaling with the number of basis functions N:
N^5 (MP2 contribution to B2-LYP) > N^3 (regular DFT)

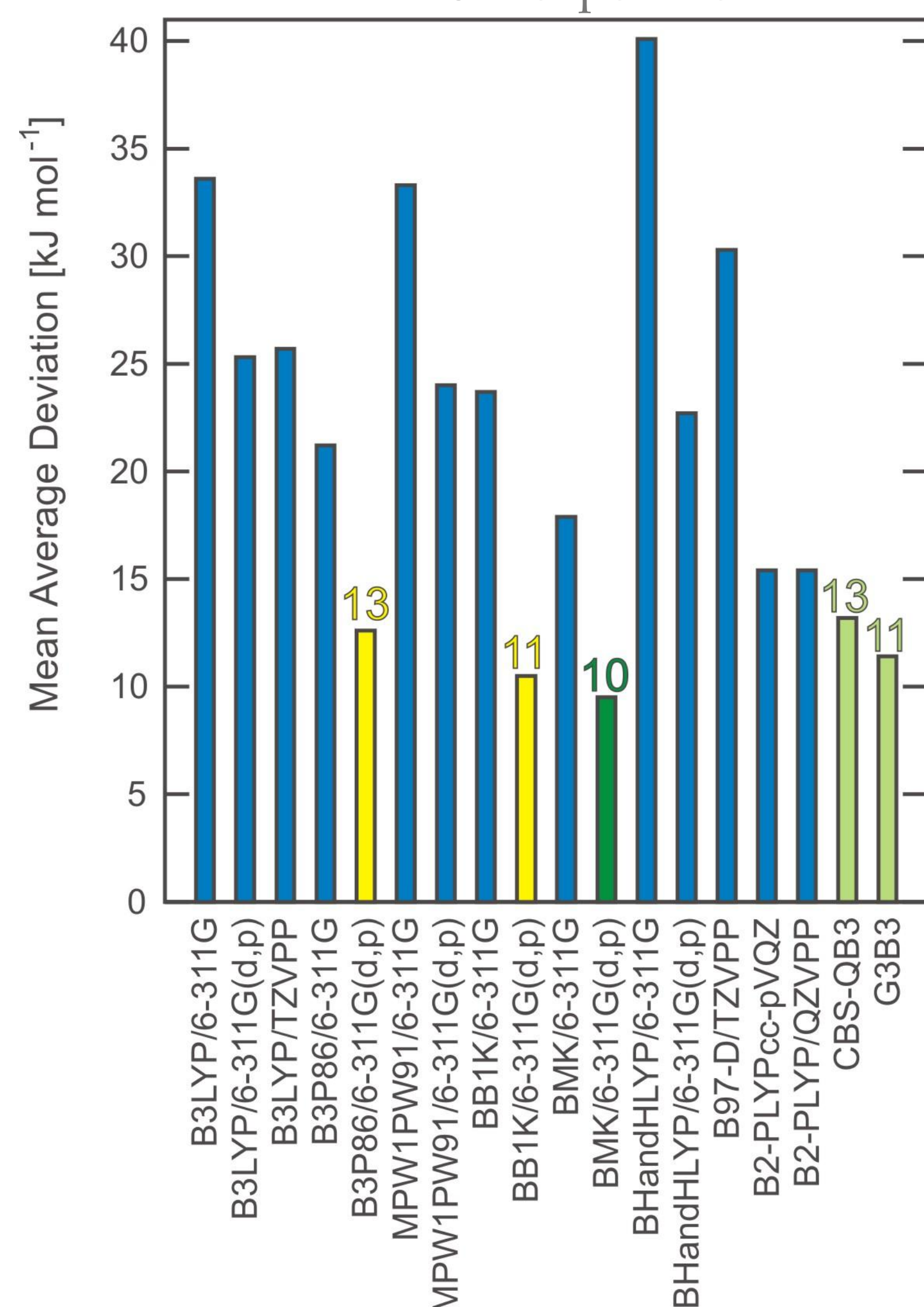→ Too computationally demanding for polymerization systems

Order of performance regular DFT:
BMK/6-311G(d,p) < MPW1PW91/6-311G(d,p) < B97-D/TZVPP

Bond dissociation enthalpies:

MAD BDE from experimental data

Mean Average Deviation [kJ mol^{-1}]

(bar labels: 13, 11, 10, 13, 11)

Best-performing DFT method: BMK/6-311G(d,p)

Good description of thermodynamics of reactions is important (see principle).

⇩

Selected cost-efficient method to study compounds and reactions involved in in-situ NMP:
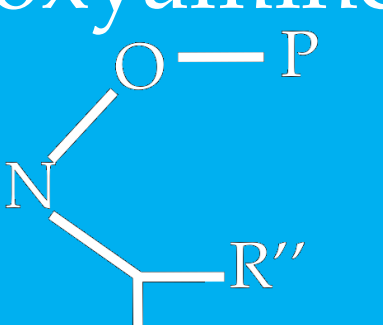BMK/6-311G(d,p)

Application: nitrone structure influences on thermodynamics and kinetics

Formation of nitroxides: addition of initiating radical to nitrone:

Nitrone	$\Delta_r H^0_{addition}$ kJ mol^{-1}	K m^{3}kmol^{-1}	log $(A/\text{m}^3\text{kmol}^{-1}\text{s}^{-1})$	E_a kJ mol^{-1}	$k_{forward}$ m^{3}kmol^{-1}s^{-1}
BBN	-90.26	1.28 10^5	4.78	58.62	3.06 10^{-6}
iPBN	-96.88	7.00 10^6	4.09	50.79	1.47 10^{-5}
PBN	-112.21	1.66 10^{10}	4.58	28.50	3.67 10^{-1}
DMPO	-141.17	1.42 10^{15}	4.75	7.61	2.49 10^3

decreasing steric hindrance: increase in nitroxide formation

Formation of alkoxyamines (in-situ): recombination of nitroxide with radical:

Alkoxyamine	P = (1)		P = (2)	
	$\Delta_r H^0_1$ kJ mol^{-1}	$K_{recomb1}=k_c/k_d$ m^{3}kmol^{-1}	$\Delta_r H^0_2$ kJ mol^{-1}	$K_{recomb2}=k_c/k_d$ m^{3}kmol^{-1}
R'=tB, R''=tB	-61.81	9.71 10^{-1}	-45.96	3.20 10^{-4}
R'=tB, R''=iP	-68.67	1.58 10^0	-94.65	6.01 10^4
R'=tB, R''=Ph	-85.03	1.46 10^3	-66.50	3.01 10^{-1}
DMPO	-116.7	5.00 10^9	-118.74	7.79 10^9

decreasing steric hindrance: increase in stability alkoxyamine

A high value of K_{recomb} corresponds with a stable alkoxyamine ⇒ slow polymer growth and resulting polymer with low number average molar mass.

Nitrone offering best trade-off between control and required polymerization time: PBN. Structural effects are in agreement with experimental findings [1].

Conclusions

A level of theory study has been performed on molecules and reactions related to in-situ Nitroxide Mediated Polymerization. The BMK/6-311G(d,p) level of theory is preferred for the description of reactions. Applying BMK to investigate the influence of the nitrone structure on elementary reactions involved in in-situ NMP, shows significant differences between the various nitrones in agreement with experimental findings.

[1] V. Sciannamea , A. Guerrero-Sanchez, U.S. Schubert , J.M. Catala , R. Jerôme, C. Detrembleur. *Polymer*, 46, 9632 (2005).