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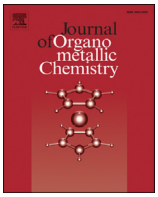

Communication

1,3-Dipolar cycloaddition of nitrones to transition metal-bound isocyanides: DFT and HSAB principle theoretical model together with analysis of vibrational spectra

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ABSTRACT

The hard and soft acids and bases (HSAB) principle together with the density functional theory (DFT) calculations were used to analyze the driving forces of the hypothetical 1,3-dipolar cycloaddition (CA) of the nitrone $CH_2{=}N(Me)O$ to the uncomplexed $C{\equiv}NMe$ and to isocyanide ligands in various transition metal complexes. The calculated activation ($\Delta G_S^{\neq}$) and reaction (ΔG_S) energies depend from the electronic chemical potential (μ), the global electrophilicity (ω) and nucleophilicity (N) indexes of the dipolarophiles, the static charge transfer "nucleophile → electrophile" (ΔN^0), and the maximum amount of electronic charge that the electrophile system may accept (ΔN_{max}). Thus, the HSAB principle may be successfully apply for the study of reactivity of such compounds. The $\Delta G_S^{\neq}$ and ΔG_S and the calculated stretching vibration frequencies $\nu(C{\equiv}N)$ of isocyanides well correlated with each other, i.e. higher values of $\nu(C{\equiv}N)$ correspond to lower values of $\Delta G_S^{\neq}$ and ΔG_S. The application of the reactivity descriptors discussed in this work is a possible alternative and a complement addition to the estimates based on the classical frontier molecular orbital (FMO) theory.

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1. Introduction

The hard and soft acids and bases (HSAB) principle [1] and its combination with the density functional theory (DFT) [2] is a powerful tool for the study of the reactivity not only in the so-called pure chemistry [3], but also in microbiology [4], toxicology [5], pharmacology and drug design [6], materials science [7], photonics [8], and heterogeneous catalysis [9]. Many examples of successful application of HSAB principle and DFT theoretical model for the investigation of various cycloaddition (CA) reactions [10] and, in particular, 1,3-dipolar CA [11] were reported in the past 15 years. Nevertheless, it was recently shown [12] that HSAB principle is not useful in the description of some cases of ambident reactivity of organic compounds, and definition of applicability limits of this method is an important theoretical task.

In continuation of the project directed toward a systematic theoretical study in the field of 1,3-dipolar CA of nitrones to isocyanide ligands [13] (Scheme 1), we carried out a study of applicability of the HSAB principle theoretical model for these processes. Such reactions comprise a potential synthetic route to N-heterocyclic carbene (NHC) complexes, i.e. compounds that may find an application in medical industry and catalysis [14], and such kind of prognostic tool as HSAB principle would be a useful addition to the FMO theory; the method traditionally used for studies of CA.

It is well known that the shift in stretching vibration frequencies $\nu(C{\equiv}N)$ in IR spectra of metal complexes featuring this structural fragment on going from uncomplexed ligand to metal-bound is often used as an indicator of the reactivity of metal complexes toward electrophilic or nucleophilic addition at the $C{\equiv}N$ bond. Our colleagues, Michelin, Pombeiro et al. established the applicability of this approach in relation to nitrile [15] and isocyanide [16] transition metal species. Considering 1,3-dipolar CA of nitrones to isocyanides as an attack of the dipole at the α-C and β-N atoms of the dipolarophile, we try to verify some correlations between values of calculated unscaled stretching vibration frequencies $\nu(C{\equiv}N)$ for the metal-free $C{\equiv}NMe$ and various isocyanide complexes, and the kinetic and thermodynamic parameters of CA.

2. Computational details

The full geometry optimization of all structures and transition states (TS) has been carried out at the DFT/HF hybrid level of theory

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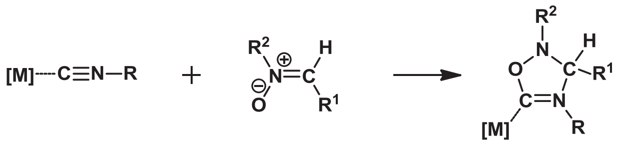

Scheme 1. 1,3-Dipolar cycloaddition of nitrones to transition metal-bound isocyanides.

using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP) [17] with the help of the Gaussian-03 [18] program package. Restricted approximations for the structures with closed electron shells and unrestricted methods for the structures with open electron shells have been employed. No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic (MWB) or relativistic (MDF) Stuttgart pseudopotentials (Ag – MWB28, Au – MWB60, Cr – MDF10, Cu – MDF10, Fe – MDF10, Mo – MWB28, Pd – MWB28, Pt – MWB60, Re – MWB60, Rh – MWB28, Ru – MWB28, W – MWB60) and the appropriate contracted basis sets [19] for the metal atoms and the 6-31G(d) basis set for other atoms. Then, single-point calculations were performed on the basis of the equilibrium geometries found using the 6-311+G(d,p) basis set for non-metal atoms. As it was shown previously [20], this approach is sufficiently accurate for the description of CAs to the C≡N bond providing results close to those obtained by the MP2, MP4, CCSD(T), CBS-Q, and G3B3 methods.

The basis set superposition error (BSSE) was not estimated because it weakly affects the activation and reaction energies of CAs to the C≡N bond, as previously indicated [20b,20c]. Furthermore, BSSE is usually less crucial for DFT-based methods compared to wave function based methods.

The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one imaginary frequency) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was studied by the analysis of vectors associated with the imaginary frequency and by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez–Schlegel method [21].

Solvent effects (δE_s) were taken into account at the single-point calculations on the basis of gas-phase geometries at the CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d) level of theory using the polarizable continuum model in the CPCM version [22] with benzene as solvent. The UAKS model was applied for the molecular cavity. The values of Gibbs free energies of activation ($\Delta G_s^{\neq}$) and reaction (ΔG_s) in solution were taken from our previous work [13] where the mathematical part of the calculation of such parameters was described in details.

The electronic chemical potential μ, chemical hardness η and softness S, global electrophilicity ω and nucleophilicity N indexes, maximum amount of electronic charge that the electrophile system may accept $\Delta N_{\max}$, and static charge transfer “nucleophile → electrophile” ΔN^0 were calculated using the following formulas [10c,23]:

$$\mu \approx \frac{E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}}{2} \tag{1}$$

$$\eta \approx E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{2}$$

$$S = \frac{1}{\eta} \tag{3}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{4}$$

$$N = E_{\mathrm{HOMO,Nu}} - E_{\mathrm{HOMO,TCNE}} \tag{5}$$

$$\Delta N_{\max} = -\frac{\mu}{\eta} \tag{6}$$

$$\Delta N^0 = \frac{\mu_{Nu} - \mu_E}{\eta_{Nu} + \eta_E}, \tag{7}$$

where E_{HOMO} and E_{LUMO} – energies of the frontier molecular orbitales, HOMO and LUMO, Nu – nucleophile, E – electrophile, TCNE – tetracyanoethylene C2(CN)4 (a reference in nucleophilicity scale proposed by Domingo and co-workers {$E_{\mathrm{HOMO,TCNE}} = -9.12$ eV – B3LYP/6-31G(d)} [10f,10g,24]. In this work, we did not consider any local reactivity descriptors [10d] (Fukui or Parr functions, local electrophilicity and nucleophilicity, etc.) because our colleagues previously demonstrated experimentally that CA of nitrones to isocyanides result in the regioselective formation of 1,2,4-oxadiazoline species [25], and later this phenomenon was proved theoretically [20a]. In addition, the local HSAB principle was originally developed for weak single site interactions [26].

The spin ground state of the $\mathrm{Re^{IV}}$ octahedral complexes was found to be a quartet, whereas the ground state of other metal complexes is a singlet, verification of the degree of purity for the spin state in case of rhenium(IV) compounds allowed the conclusion that the maximum overstatement calculated eigen value of the square of the total spin of the system $<\hat{S}^2>$ compared with the theoretically expected value $<\hat{S}^2_{\mathrm{theory}}> = S(S+1)$, where S – total spin of the system, is only 4%.

3. Results and discussion

To investigate from HSAB principle theoretical model viewpoint 1,3-dipolar CA of the nitrone $CH_2{=}N(Me)O$ to isocyanide ligands in transition metal complexes we calculated some main global reactivity indexes for such species. The values of these parameters are presented in Table 1S (see Supporting information).

Based on the classification proposed by Domingo et al. (electrophiles: $\omega \geq 1.50$ eV – strong, $1.50 > \omega > 0.80$ eV – moderate, $\omega \leq 0.80$ eV – marginal; nucleophiles: $N \geq 3.00$ eV – strong, $3.00 > N > 2.00$ eV – moderate, $N < 2.00$ eV – marginal) [10c,24,27], the nitrone molecule $CH_2{=}N(Me)O$ can be attributed as a moderate electrophile and a strong nucleophile, whereas the uncomplexed C≡NMe (**L**) is both marginal electrophile and nucleophile. The transition metal isocyanide complexes **1a**–**1s** can be divided into two groups as electrophiles (**1c**, **1e**–**1f**, **1i**–**1r** are strong and **1a**–**1b**, **1d**, **1g**–**1h**, **1s** are moderate) and into three groups as nucleophiles (**1b**–**1d**, **1g**–**1h**, **1p**, **1s** are strong, **1a**, **1e**–**1f**, **1i**–**1l**, **1n**–**1o**, **1q** are moderate, and **1m** is marginal). Taking into account that in polar processes the charge transfer always fluxes from the species with higher μ (the nucleophile) to the species with lower μ (the electrophile) [24], we treated the metal-free isocyanide (**L**) and complexes **1a**–**1c**, **1e**–**1g**, **1i**–**1r** as formal electrophiles, whereas complexes **1d**, **1h**, **1s** as formal nucleophiles with respect to the nitrone $CH_2{=}N(Me)O$. We did not detect any relationships between ω and N for a series of 20 isocyanide species **L** and **1a**–**1s** (Fig. 1, A). Considering as a criterion for polarity of CA the static charge transfer “nucleophile → electrophile”, it is noteworthy that

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