

***Ab initio* Study of RNCN (R = H, F, Cl, Br, CH₃) Radicals Plus NO Reaction: Kinetics, Mechanism and Product Branching Probabilities**

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Abstract. We carried out a computational study of radical reactions of RNCN (R = H, F, Cl, Br, CH₃) + NO to investigate how the substitution can influence their corresponding energy barriers and rate coefficients. The preferable reactive sites of RNCN radicals with various substituents are calculated by employing the Fukui functions and hard-and-soft acid-and-base theory, which were generally proved to be successful in the prediction and interpretation of regioselectivity in various types of electrophilic and nucleophilic reactions. Based on our calculated results, we found that the largest values of Fukui function are mostly located on the unsubstituted nitrogen atom (N_t), which accounts for the preferable reactive site usually occurring N_t atom in most of the substituted RNCN radicals, although the CH₃-substituted one is an exception. Our calculated results clearly show that if the substituted RNCN radical has electron-donating substituent, its corresponding barrier heights for transition states will be substantially decreased. We also used the RRKM theory to predict the kinetic data. As it could be expected, the total rate constants obviously become greatly enhanced with electron-donating substituent (CH₃-substituted species). In addition, the values of k_{total} for all substituted RNCN will initially decrease with increasing temperature. Nevertheless, these behaviors will be inverted at higher temperature and the values of k_{total} become positive temperature dependence.

Keywords: DFT, HNCN, Substitution, RRKM.

1. Introduction

The production of nitrogen oxides (NO_x) via the combustion of fossil fuels attracts great interest as these oxides are toxic pollutants in the atmosphere [1]. Therefore, the mechanisms and rate parameters for reactions involving nitrogen compounds have been extensively investigated in relation to such air pollutants. Numerous authors have reported theoretical and experimental approaches to eliminate NO [2-9], many of which employ cyanogen species as an effective reagent to remove NO. Our aim in this research is to discover the probable reactants which might react with NO to form the stable product such as N₂ which is not pernicious to our surroundings and perhaps with lower reaction barriers. From our previously published work on HNCN + NO reaction [7], our results indicated the favorable pathways for the formation of several isomers of an HNCN-NO complex. Formations of HNC + N₂O (**P1**) and HNCO + N₂ (**P2**) are also feasible since these two pathways involve transition states with very small/low activation energies. In this paper, we further studied a series of substituted RNCN (R = H, F, Cl, Br, CH₃) radicals reacting with NO and discussed the product selectivity exhibited in various types of electrophilic and nucleophilic reactions. Besides, we carried out variational transition-state theory (VTST) and microcanonical Rice-Ramsperger-Kassel-Marcus (RRKM) [10-13] theory based on the energies and structures predicted by a high-level *ab initio* method.

2. Computational Method

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We carried out the quantum mechanical calculations by using the Gaussian 03 program package [14]. The stationary points on the potential energy surfaces for the RNCN + NO reactions were optimized by density functional theory with the Becke three-parameter hybrid method and the Lee-Yang-Parr correlation functional approximation (B3LYP) [15-16]. Basis sets with increasing accuracy of polarized split-valence and diffuse functions for heavy and hydrogen atoms 6-311++G(3df,2p) were used in the calculations. Frequency calculations were performed at the same level to check whether the obtained equilibrium structures are local minima or saddle points. Among which, the reactants, intermediates and products possess all real frequencies, whereas transition states have only one imaginary frequency. Zero-point energy (ZPE) corrections are also considered at B3LYP/6-311++G(3df,2p) level. Intrinsic reaction coordinate (IRC) calculations were also performed to confirm the connection between the transition state and the designated intermediates. To obtain trustworthy energies, we perform single-point calculations employing a coupled-cluster technique with single and double excitations and evaluations by perturbation theory of triple contributions CCSD(T) [17] based on the geometries optimized at the B3LYP/6-311++G(3df,2p) level. The highest level of theory used in this work is thus denoted CCSD(T)/aug-cc-PVQZ//B3LYP/6-311++G(3df,2p). Unless otherwise specified, the CCSD(T) single-point energies are used in the following discussion. The rate constants for the principal product channels are predicted with the VTST and RRKM theory using the VariFlex program [18].

3. Results and Discussion

Our first step in studying this reaction was to categorize the roles of RNCN and NO in the reaction. Here, we applied the Mulliken DA (donor-acceptor) theory [19] to explore the reaction behaviors in various types of electrophilic and nucleophilic substituents. We arbitrarily denote the RNCN radical as D and the NO radical as A. Thus, D^+A^- and D^-A^+ represent the charge-transfer configurations from D to A and A to D, respectively. We employed B3LYP/6-311++G(3df,2p) level of theory to calculate the adiabatic IE (ionization energy) and EA (electron affinity) for both RNCN and NO, and the results are shown in Table 1. The charge-transfer energies of D^+A^- and D^-A^+ are calculated as $D^+A^- = IE_{RNCN} - EA_{NO}$ and $D^-A^+ = IE_{NO} - EA_{RNCN}$, respectively. As shown in Table 1, the charge-transfer energies of D^+A^- (ca. 9.7~11.1) are much smaller than those of D^-A^+ (ca. 12.0~12.8), which demonstrate that the process of charge transfer from RNCN radicals to NO is more likely to take place. Besides, the fluctuation of the D^+A^- values within a small range in the Table also reasonably represents the substitution effect from the substituted RNCN. An investigation of these data shows that it is satisfactory to believe that the RNCN radicals exhibit a nucleophilic characteristic toward the reaction of NO.

Table 1: The Calculated Ionization Energies (IE)^a, Electron Affinities (EA)^a, and Charge-Transfer Energies Corresponding to the States (D^+A^- and D^-A^+)^b of NO Attack on the Substituted RNCN Radicals (R = H, F, Cl, Br, and CH₃); D represents RNCN, and A for NO

Structure	IE	EA	D^+A^-	D^-A^+
NO	9.72	0.95		
HNCN	11.97	-2.55	11.02	12.27
FNCN	12.09	-3.00	11.14	12.72
CINCN	11.09	-3.04	10.14	12.76
BrNCN	10.80	-3.08	9.85	12.80
CH ₃ NCN	10.60	-2.30	9.65	12.02

^a B3LYP/6-311++G(3df,2p) adiabatic ionization energies (IE) and electron affinities (EA) of RNCN and NO radicals in eV.

^b Charge-transfer energies of D^+A^- and D^-A^+ states, calculated according to following formalisms $D^+A^- = IE_{RNCN} - EA_{NO}$, $D^-A^+ = IE_{NO} - EA_{RNCN}$.

From our previous published work of HNCN + NO reaction, our calculated results indicate that the most favorable pathway is the formation of HNC + N₂O (**P1**) product since this path is almost barrierless. Formation of HNCO + N₂ (**P2**) is also feasible even though this pathway involve little activation energy. Therefore, in this study we mainly examined the substitution effects in these two paths, **Reactant**→**RIM1**→**RTS2**→**RP1** and **Reactant**→**RIM1**→**RTS3**→**RIM6**→**RTS9**→**RP2** (as shown in Figure 1), trying to find out how the substitution effect can influence their corresponding energy barriers. The potential energy surfaces calculated at the CCSD(T)/aug-cc-PVQZ//B3LYP/6-311++G(3df,2p) level are shown in Figure 2. We prefixed the letter R to reactant (HNCN), **RIM1**, **RIM6**, **RTS2**, **RTS3** and so forth to represent the F-,

Cl-, Br-, and CH₃-substituted species. The existence of the substituent remarkably distinguishes the two nitrogen atoms of the RNCN molecule, which could provide the product selectivity in this particular reaction.

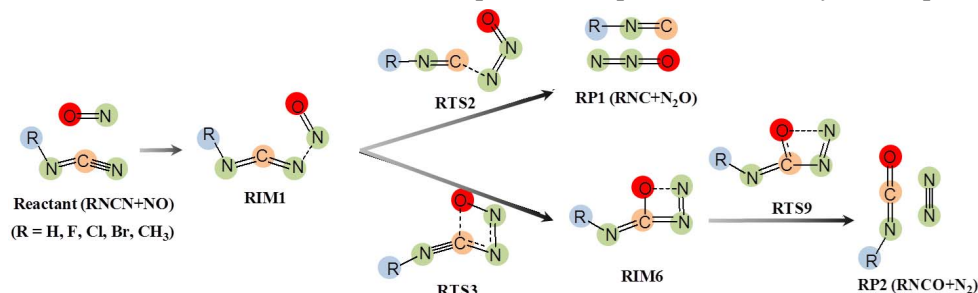


Fig. 1: The two principal pathways for the RNCN plus NO reactions, where R = H, F, Cl, Br, and CH₃.

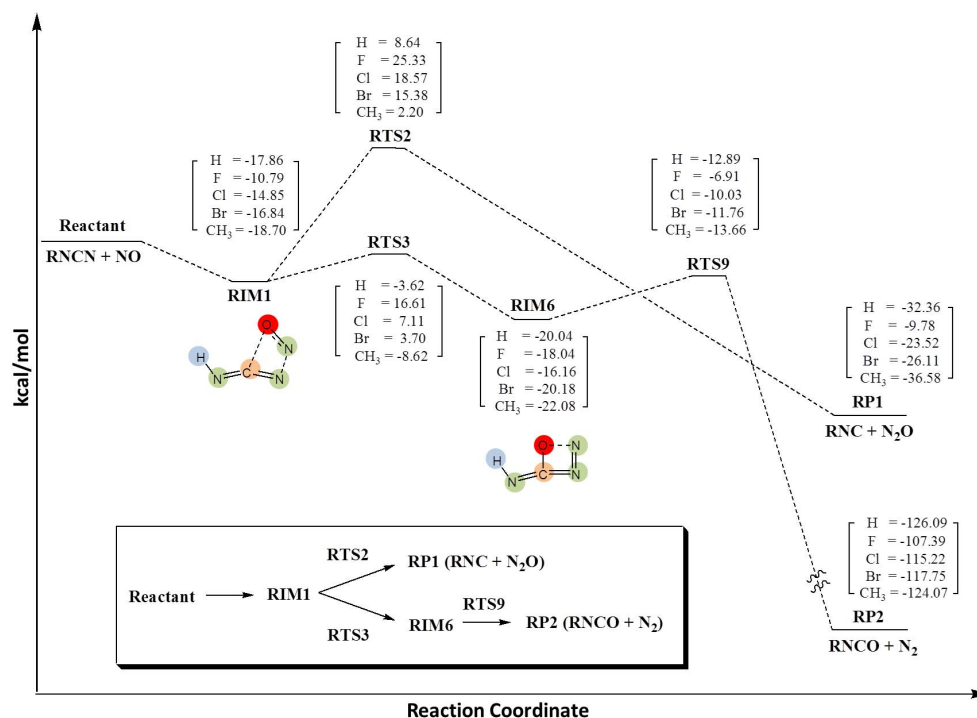


Fig. 2: Calculated profiles of potential energy diagram for two main paths in RNCN+NO reaction at the CCSD(T)/aug-cc-pVQZ//B3LYP/6-311++G(3df,2p) level.

In addition, to be more specific, we apply the Fukui function and hard-and-soft acid-and-base (HSAB) principles to prove the regioselectivity [20]. Gázquez et al. [21] also pointed out in their derivation of the equation of interaction energy in terms of the condensed Fukui function and local softness of an atom in the molecule that the largest value of the Fukui function is, in general, associated with the most reactive site. In our calculation for N electrons in a system, independent calculations are made for the corresponding $(N - 1)$, N , and $(N + 1)$ electron systems with the same geometry. A natural population analysis yields $q_k(N - 1)$, $q_k(N)$, and $q_k(N + 1)$ for the predicted possible sites of reaction of RNCN and NO molecules, and the Fukui function is calculated as a difference of population between N and $N + 1$ or N and $N - 1$ electron systems. We will choose the f^0 value for comparison since this title reaction is more representative of a radical system. Based on our calculated data in Table 3, it is found that the largest values of Fukui function are mostly located on the N_t atoms (the subscript t symbol signifies the terminal N atom of RNCN), which accounts for the preferable reactive site usually occurring on the unsubstituted nitrogen atom (N_t) in most of the substituted RNCN radicals, although the CH₃-substituted one is an exception. However, for methyl substitution of CH₃CNCN, the Fukui function of N_t , 0.410, is still competitive with that of N , 0.423. In addition, applying the HSAB theory we found that the largest values for the local softness s^0 for all reactants are on the N_t atom of RNCN and the N atom of NO, which also accounts for the favorable formation of the adducts of RIM1 (see Figure 1). In contrast, the Fukui function and local softness calculated to be smallest, f

$^0 = 0.372$ and $s^0 = 1.155$, of the O atom in NO, indicating an unfavorable addition through its O-terminus site is thus readily explained.

Table 3: The Condensed Fukui Functions for the N, C, and N_t Atoms in RNCN Radicals (R = H, F, Cl, Br, and CH₃), and N and O Atoms in NO, as well as the Global and Local Softness of the Molecules Calculated at B3LYP/6-311++G(3df, 2p) Level

Molecule	f^0 ^a				Global softness S^c	Local softness (s^0) ^d			
	N	C	N _t ^b	O		N _c ^a	C	N _t ^b	O
NO	0.628			0.372	3.104	1.949			1.155
HNCN	0.481	0.022	0.488		1.874	0.901	0.041	0.914	
FNCN	0.406	0.016	0.469		1.803	0.732	0.029	0.846	
CINCN	0.348	0.026	0.371		1.925	0.670	0.050	0.714	
BrNCN	0.305	0.024	0.355		1.960	0.598	0.047	0.696	
CH ₃ NCN	0.423	0.027	0.410		2.109	0.892	0.057	0.865	

^a Atomic charges according to a natural population analysis.

^b N_t signifies the terminal N atom of RNCN.

^c $S = 1/(IE - EA)$, with ionization energy IE and electron affinity EA; the energy unit is hartree.

Microcanonical RRKM calculations for the RNCN + NO (R = H, F, Cl, Br, CH₃) reactions were performed by solving the master equation⁴⁶ involving multistep vibrational energy transfer for the excited intermediates (RNCN-NO) for the dissociation processes. The predicted values for total rate constants ($k_{total} = k_{M1} + k_{P1} + k_{P2}$) for reaction of RNCN+NO (R = H, F, Cl, Br, CH₃) at Ar pressure of 760 torr in the temperature range of 298-3000 K are shown in Figure 3. As it could be expected, the total rate constants obviously become greatly enhanced with electron-donating substituent (CH₃-substituted species). In addition, the values of k_{total} for all substituted RNCN will initially decrease with increasing temperature. Nevertheless, these behaviors will be inverted at higher temperature and the values of k_{total} become positive temperature dependence. The results could imply that, at lower temperatures, all substituted intermediates RNCN-NO (**RIM1**) can be stably formed from RNCN + NO, which need to be experimentally confirmed. In the higher temperature range, however, dissociation rate becomes the most significant contribution and the formations of **RP1** and **RP2** will take place promptly at this circumstance.

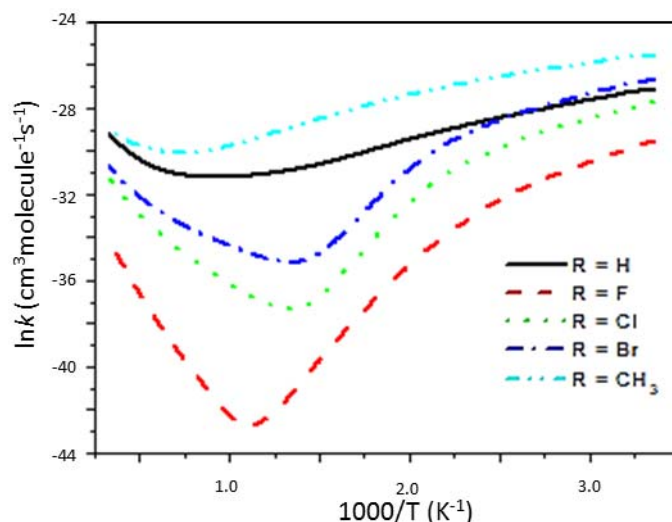


Fig. 3: The predicted total rate constants ($k_{total} = k_{M1} + k_{P1} + k_{P2}$) for reaction of RNCN+NO (R = H, F, Cl, Br, CH₃) at Ar pressure of 760 torr in the temperature range of 298-3000 K.

4. Summary

In this work, we have presented a direct computational study on the reaction mechanisms and kinetics for the RNCN+NO (R = H, F, Cl, Br, CH₃) reactions using the high level CCSD(T) approach. Four different substituents show diverse reactivity in the process of RNCN + NO, and these radical reactions will favor the RP2 (RNCO + N₂) formation pathway, no matter whether electron-donating or withdrawing substituents are present. Based on the results from Fukui functions and HSAB theory, it is found that the largest values of

Fukui function are mostly located on the N_t atoms, which accounts for the preferable reactive site usually occurring on the unsubstituted nitrogen atom (N_t) in most of the substituted RNCN. The equations for the individual and total rate constants are given for all substituted RNCN + NO systems, and these critical reactions may be employed for a more realistic combustion kinetic modeling applications.

5. References

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