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Prahlad Roy Chowdhury, D Monali Kawade and G. Naresh Patwari **D**

The NO release following 266 nm photolysis of ortho and meta isomers of nitrophenol and nitroaniline shows a bimodal translational energy distribution, wherein the slow and fast components originate from dynamics in the So and T1 states, respectively. The translational energy distribution profiles for any NO product state show a higher slow-to-fast (s/f) branching ratio for the ortho isomer in comparison with the meta isomer. The observed variation in the s/f branching ratio vis-à-vis the ortho and meta isomers is attributed to the presence of intramolecular hydrogen bonding between the ortho substituent and NO2 moiety, which favours the roaming mechanism.

Nitroaromatic compounds produce nitric oxide (NO) upon irradiation, which modulates the oxidative capacity of the atmosphere. 1,2 Measurements on the translational energy distribution of NO fragments following UV photolysis of nitroaromatic compounds show the presence of slow and fast components (a bimodal behaviour), which has been interpreted as the presence of two distinct pathways for NO release.^{3,4} The absence of a direct route to produce NO from nitroaromatic compounds suggests that both pathways must proceed via nitro-to-nitrite photoisomerization. The 266 nm excitation of nitrobenzene to high-lying electronic states (S₄/S₃) results in ultrafast relaxation to the T1 state with a timescale of about 200 fs, and thereafter the dynamics on the T₁ surface is much slower with the lifetime of about 90 ps, wherein the nuclear dynamics will dominate.⁵ These observations are in accordance with the hypothesis that the topography of the T₁ surface influences the dynamics of NO formation.³ Based on electronic structure calculations, the fast NO component is attributed to a direct elimination channel from the T1 state featuring an oxaziridine ring-type (tight) transition state.3,4,6 On the other hand, the slow translational energy component of the NO

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India. E-mail: naresh@chem.iitb.ac.in

† Electronic supplementary information (ESI) available: Methodology, 2D-PES at the M0-62X/6-311++G (d,p) level, one dimensional cut of the T1-2D-PES along the MEP of NO release, VMI images and fitting of the $[P(E_T)]$ profiles, and T_1/S_0 crossing in nitroaniline. See DOI: https://doi.org/10.1039/d4cc01497a

radical is attributed to nitro-to-nitrite photoisomerization in the ground state, either arising from an oxaziridine ring-type and/or a NO2 roaming transition state. The NO2 roaming mechanism originates from the frustrated dissociation of the C-N bond in nitrobenzene and the NO2 radical is trapped in a shallow potential well around the phenyl radical and "roams" to form phenyl nitrite (C₆H₅ONO), and the release of NO radical with low translational energy is attributed to the presence of an exit barrier for O-NO bond dissociation.4 Thus far, it has been inferred that the slow translational energy component of the NO radical originates from the So state with both roaming and non-roaming (oxaziridine ring-type) mechanisms. Recent highlevel electronic structure calculations have suggested that the topography of the T₁/S₀ crossing points influences the slow and fast translational energy components of NO, which could involve oxaziridine or roaming-type geometries, and the roaming pathway has a relatively higher (4.61 eV) barrier.⁷

The ability of T₁ surface topography to direct the NO release via the oxaziridine or roaming-type mechanisms, and thereby influence the relative yields of the fast and slow translational energy components, was investigated in several orthosubstituted nitrobenzenes by probing a specific NO fragment (v = 1; I = 50.5) state.⁸ In these cases the appearance of the bimodal translation energy distribution profile of the NO radical was dependent on the nature of the substituent. The substituents that were capable of forming intramolecular hydrogen bonding with the NO2 group, such as OH and NH2 groups, favoured the slow component over the fast component. In other words, the slow-to-fast (s/f) branching ratio between the components of the total translation energy distribution profile of NO was greater than one (s/f > 1) in the case of o-nitrophenol and o-nitroaniline. On the other hand, a reverse trend with s/f < 1 was observed for o-nitroanisole and o-nitrotoluene, wherein the substituents do not hydrogen bond with NO2. The experimentally observed results were interpreted on the basis of two-dimensional potential energy surfaces (2D-PESs) in the T_1 state and it was inferred that the minimum energy path favours the NO2 roaming mechanism for the

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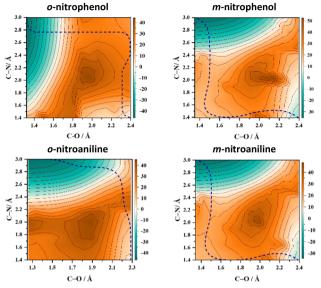


Fig. 1 Two-dimensional potential energy surface (2D-PES) plots of onitrophenol, m-nitrophenol, o-nitroaniline, and m-nitroaniline calculated using the B3LYP/6-311++G(d,p) level of theory. The blue dashed lines represent the minimum energy paths (MEPs) connecting the starting structure (bottom right corner) with the formation of NO and the cofragment phenoxy radical (top left corner) in the T_1 state. The energy scale is in kcal mol⁻¹ relative to the starting geometry on the T_1 surface. The one-dimensional cut of the 2D-PES along the minimum energy path resulting in NO release is shown in Fig. S1 (ESI†) along with the selected geometries.

substituents, in the *ortho* position, capable of hydrogen bonding (OH and NH₂), while in the other cases (H, CH₃, OCH₃ and CF₃ groups), the NO release *via* an oxaziridine ring-type mechanism is preferred.⁸ On the other hand, the variation in the substituents at the *para* position had only a marginal influence on the s/f branching ratio.⁹

A pertinent question that arises at this state is: does the intramolecular hydrogen bonding between the NO2 and the ortho substituent influence the NO release mechanism? To test this hypothesis 2D-PESs in the T₁ state were calculated for two pairs of substituted nitrobenzenes in which the OH and NH₂ groups were switched from the ortho position to the meta position and the corresponding 2D-PESs in the T1 state are shown in Fig. 1 and Fig. S2 (ESI†). These 2D-PESs clearly illustrate that the minimum energy path switches from the NO₂ roaming mechanism to the oxaziridine ring-type mechanism for both OH and NH2 substituents when shifted from the ortho to meta position, respectively. The topographical aspects of the 2D-PESs remained unaltered with two distinct DFT functionals viz., B3LYP and M06-2X (compare Fig. 1 and Fig. S2, ESI†). Since the 2D-PES is the projection of the multidimensional potential on two nascent internal coordinates leading to NO release, it can be therefore hypothesised based on the minimum energy pathway in the 2D-PESs that the s/f ratio will be higher in the ortho isomer in comparison with the meta isomer.8

The experimental realization of this conjecture based on the 2D-PES calculation was carried out by measuring the total

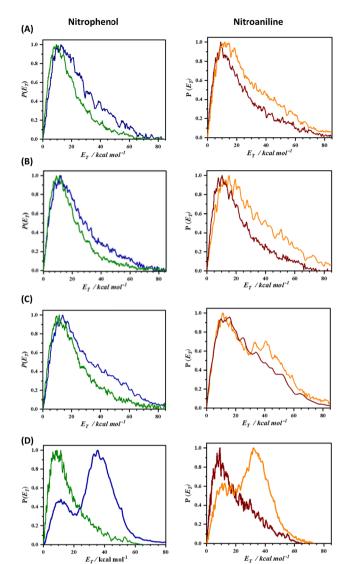


Fig. 2 The total translational energy distribution profiles $[P(E_T)]$ of NO, produced from nitrophenol (left panel) and nitroaniline (right panel), probed for various product states of NO (A) v=0; J=21.5, (B) v=0; J=29.5, (C) v=0; J=33.5 and (D) v=1; J=50.5. The $[P(E_T)]$ profiles of the *ortho* and *meta* nitrophenols are depicted by solid green and blue curves, respectively, while *ortho* and *meta* nitroanilines are represented by solid brown and orange curves, respectively. It is noteworthy that the fast component in the $[P(E_T)]$ profiles of *meta* isomers is consistently higher than that of the *ortho* isomer across all the product states.

translational energy distribution profiles of NO produced from *o*-nitrophenol, *m*-nitrophenol, *o*-nitroaniline, and *m*-nitroaniline using the velocity map imaging (VMI) technique¹⁰ and the results are presented in Fig. 2. In all the four NO product states that were probed, the translational energy distribution profiles show bimodal behaviour (see Fig. S3 and S4, ESI†) with the s/f branching ratio for the *ortho* isomer higher than the corresponding *meta* isomer (see Table 1). Additionally, the s/f ratio of *o*-nitrophenol is always higher than the *o*-nitroaniline, which is in accordance with the fact that the OH group forms stronger hydrogen bonds than the NH₂ group. These observations clearly reinforce the role of intramolecular hydrogen bonding in

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Table 1 Slow-to-fast (s/f) branching ratios for various NO product states

NO product state	Nitrophenol		Nitroaniline	
	ortho	meta	ortho	meta
v = 0; J = 21.5	4.92	3.17	3.23	2.28
v = 0; J = 29.5	5.40	3.78	3.67	2.38
v = 0; J = 33.5	4.31	2.31	2.05	1.21
$\nu = 1; J = 50.5$	3.85	0.33	1.92	0.45

favouring the slow component. In general, the contribution from the fast component increases with rotational quantum number J, in agreement with the earlier reports; 4 however, this effect appears to be more prominent with an increase in vibrational quantum number v. It must be noted that the 2D-PES is a projection of the multidimensional potential in two-dimensions and hence a simplified model. The trends in the s/f branching ratio, therefore, are an indicator of the influence of the substituent to form intramolecular hydrogen bonding with the NO₂ group resulting in the enhancement of the roaming mechanism, thereby validating the initial hypothesis.

The topology of the T₁ surface regulates the preferential mechanism; however, it has been well established that the nature of the T₁/S₀ crossing points and the exit barrier on the S₀ surface dictate the translational energy of the NO products. 4,5,11-14 In order to assess the role of the So surface on the translational energy distribution of the NO products, 2D-PESs in the S₀ state were also computed, which are depicted in Fig. 3 (and Fig. S5, ESI†). In the case of *o*-nitrophenol, an early (closer to the reactant) T_1/S_0 crossing point along the minimum energy path on the T_1 surface is a loose transition state, reflecting the NO2 roaming mechanism. The NO₂ roaming and the oxaziridine mechanism are distinguished by evaluating the difference between the two N-O bonds, which is depicted in Fig. S6 (ESI†). The roaming path is characterized by a sudden and late change in the difference between two N-O bonds, whereas the oxaziridine pathway is more gradual. On the So 2D-PES, the pathway for NO release is corrugated with an exit barrier of about 14 kcal mol⁻¹ (see Fig. 3) and the presence of several phenyl nitrite like intermediates, which ultimately result in slow NO release. Conversely, in the case of m-nitrophenol, a late (closer to the products) T₁/S₀ crossing point was observed along the minimum energy path on the T₁ surface, which leads to the fast translational energy component. The slow translational energy component of the NO release is generally attributed to the dynamics on the S₀ surface, which once again originates from the roaming and non-roaming mechanisms. Therefore, based on the present set of results, it can be inferred that intramolecular hydrogen bonding between the NO2 and the substituent in the ortho position plays a pivotal role in enhancing the roaming mechanism, thereby resulting in a higher s/f ratio for the ortho isomer relative to the meta isomer as well as higher s/f ratio for the o-nitrophenol in comparison with o-nitroaniline.

Summarising, the branching ratio of the slow-to-fast (s/f) translational energy components, for various NO product states, shows a higher value for the ortho isomer in comparison to the meta isomer. Furthermore, consistently higher s/f ratio

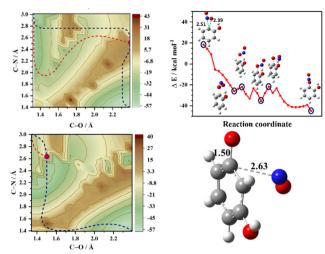


Fig. 3 Ground state (S_0) 2D-PES plots of o-nitrophenol (top left) and mnitrophenol (bottom left) with the projected minimum energy path (MEP) that connects the reactant (bottom right corner) to the NO and phenoxy radical as products (top left corner) in the T_1 state (blue dashed line). The purple dot represents the T_1/S_0 crossing point along the T_1 MEP and the red dashed lines represent the MEPs in the S_0 state. Note that the T_1/S_0 crossing for onitrophenol and m-nitrophenol is early and late relative to the reactant, respectively. The S₀-MEP and selected structures after the T₁/S₀ crossing point for o-nitrophenol are shown (top right) along with the T₁/S₀ crossing point of m-nitrophenol (bottom right). The distances are shown in Å and the energy scale is in kcal mol⁻¹ relative to the starting geometry in the T₁ state.

for the o-nitrophenol over o-nitroaniline is attributed to the OH group's propensity to form stronger hydrogen bonds compared to the NH₂ group. Therefore, it is inferred that the *ortho* isomer preferentially releases the slower NO fragments, which is attributed to the minimum energy roaming path. On the other hand, in the meta isomers, the faster component mediated via the oxaziridine pathway is enhanced. Thus, it has been illustrated that the hydrogen bonding ability of the substituent in the ortho position to the NO₂ group favours the roaming mechanism.

A skimmed molecular beam of helium doped with the heated (330–350 K) reagents (o-nitrophenol, m-nitrophenol, onitroaniline, and m-nitroaniline; Sigma Aldrich) was intersected by a counter-propagating pump (266 nm) and probe lasers15 and the ensuing NO cations were detected via the $A^2\Pi - (X^2\Pi) [(0,0); Q_1 (J = 21.5; 29.5; 33.5)]$ and $A^2\Pi - (X^2\Pi)$ $[(1,0); P_1 J = 50.5]^{16,17}$ and imaged. Each image was collected for 50 000 shots, which were symmetrized using ImageJ software. 18 Abel inversion was carried out by the Basis Set Expansion method (BASEX) to extract the translational energy distribution.¹⁹ The plane of polarization of both lasers is kept parallel to the plane of the detector and the laser flux was optimized such that the signal intensity for the NO fragment was observed only in the presence of both the pump and probe lasers. The total translational energy profiles $[P(E_T)]$, black traces in Fig. S3 and S4 (ESI†), were fitted to a bimodal empirical function, 8,20,21

$$P(E_{\rm T}) = C \cdot [(E_{\rm T})^{a_1} \cdot (E_{\rm T}^{\rm max} - E_{\rm T})^{b_1} + (E_{\rm T})^{a_2} \cdot (E_{\rm T}^{\rm max} - E_{\rm T})^{b_2}]$$

where a_1 , a_2 , b_1 , and b_2 are adjustable parameters, C is a normalization constant, and $E_{\mathrm{T}}^{\mathrm{max}}$ is the maximum total Communication ChemComm

translational kinetic energy available for the fragments in the centre-of-mass frame after dissociation.

The experimental results were interpreted by calculating the two-dimensional potential energy surfaces (2D-PES) in the ground (S₀) and first excited triplet (T₁) states with the B3LYP/6-311++G(d,p) and M06-2X/6-311++G(d,p) levels of theory using the Gaussian 09 suite of programs.²² The 2D-PESs were mapped along two internal coordinates; the C-N bond ("C" referring to the carbon atom of the aromatic ring to which the nitrogen atom "N" of the nitro group is attached) and C-O bond ("O" referring to the oxygen atom of the nitro group that is away from the ortho substitution, which later forms a bond with the "C" atom of the aromatic ring leading to NO release). The distances $R_{(C-N)}$ and $R_{\rm (C-O)}$ are varied in the range 1.4 to 3.0 Å and 1.25 to 2.3 Å, respectively, in 14 equidistant steps on each coordinate resulting in 196 data points. The minimum energy path on the 2D-PES for the release of NO from each of the substituted nitrobenzenes was evaluated using the Minimum Energy Path Surface Analysis (MEPSA) tool.²³

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Conflicts of interest

The authors declare no conflict of interest.

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