Supplementary Information

S1. Simulation of the translational exothermicity spectrum.

To model the translational exothermicity ΔE_T of a non-dissociative SET reaction, we need to know the probability of forming the two product NO^+ ions in the various accessible combinations of electronic states after the interaction of NO^{2+} and NO. We determine this probability P using an extension of a simple model which has been presented before.[7] Specifically, we have:

$$P[NO^{2+}(v^{++}), NO^+(Z, v_c), NO^+(Y, v_e)] = LZP \times P_e[NO \rightarrow NO^+(Y, v_e)] \times P_c[NO^{2+}(v^{++}) \rightarrow NO^+(Z, v_c)] \quad (1)$$

Here, $P[NO^{2+}(v^{++}), NO^+(Z, v_c), NO^+(Y, v_e)]$ represents the probability of a SET transition from NO^{2+} in its ground electronic state and vibrational level v^{++} to capture and ejection ions in electronic states Z and Y and vibrational levels v_c and v_e respectively. LZP is the Landau-Zener transition probability for crossing from the reactant NO^{2+} + NO potential energy curve (PEC) to the $NO^+(Z)$ + $NO^+(Y)$ PEC. In equation (1), $P[NO \rightarrow NO^+(Y, v_e)]$ is the probability of forming the ejection NO^+ in the (Y, v_e) vibronic state from neutral NO and $P[NO^{2+}(v^{++}) \rightarrow NO^+(Z, v_c)]$ is the probability of forming the capture ion in $NO^+(Z, v_c)$ from $NO^{2+}(v^{++})$. The transition probabilities for the capture and ejection transitions can be decomposed into electronic and vibrational components. Specifically, for the ejection transition:

$$P_e[NO \rightarrow NO^+(Y,v_e)] = ETF[NO \rightarrow NO^+(Y)] \times FCF(0,v_e) \quad (2)$$

In equation (2), $ETF[NO \rightarrow NO^+(Z)]$ is the electronic transition probability for going from NO in the ground electronic state to the $NO^+(Z)$ electronic state and $FCF(0,v_e)$ is the Franck-Condon factor for the transition from the ground vibronic level of NO to the vibrational level v_e in NO^+(Z). For this transition, in our collision system, we know that the neutral reactant is in its ground electronic ($^2\Pi$) and vibrational state, neglecting any spin-orbit splitting, as this collision partner is admitted as an effusive beam at room temperature. The values of $FCF(0,v_e)$ were obtained using the LEVEL programme of Le Roy with constants derived from calculated PECs of the accessible NO^+ electronic states.[33, 43] $ETF[NO \rightarrow NO^+(Z)]$ was estimated from the relative band intensities of the electronic transitions observed in the NO photoelectron spectrum recorded at 25 eV.[13] In this spectrum the most intense transition is to $NO^+(b, 2s\sigma^{*2}\ 2p\sigma^1\ 2p\pi^4\ 2p\pi^{*1})$ with the formation of $NO^+(X, 2s\sigma^{*2}\ 2p\sigma^2\ 2p\pi^4\ 2p\pi^{*0})$ and $NO^+(A, 2s\sigma^{*2}\ 2p\sigma^1\ 2p\pi^4\ 2p\pi^{*1})$ states about half as probable. All three of these transitions involve one-electron ejection processes from the ground electronic state of NO $(2s\sigma^{*2}\ 2p\sigma^2\ 2p\pi^4\ 2p\pi^{*1})$.[40] All other electronic transitions between NO and NO^+ are much weaker and so are assigned an ETF of zero.

The probability of the capture transition is calculated in a similar way to that of the ejection transition:

$$P_c[\mathrm{NO}^{2+}(v^{++})\rightarrow\mathrm{NO}^{+}(Z,v_\mathrm{c})] = ETF[\mathrm{NO}^{2+} \rightarrow \mathrm{NO}^{+}(Z)] \times FCF(v^{++},v_\mathrm{c}) \quad (3)$$

Although studies of double-photoionization of NO show that higher electronic states of NO^{2+} are populated in double ionization events, we expect the relaxation of these states to occur on the time-scale (100μs) of our experiments.[44] Hence, we assume all the NO^{2+} reactants are in their electronic ground state. Again, we calculate the FCFs using the LEVEL programme and available PECs.[33, 42-43] The electronic transition probability in equation (3), $ETF[\mathrm{NO}^{2+} \rightarrow \mathrm{NO}^{+}(\mathrm{Z})]$, was modelled assuming that single-electron transitions dominate. Given that the ground $^2\Sigma_g^+$ electronic state of the dication has the electronic configuration $(2s\sigma^{*2}\ 2p\pi^4\ 2p\sigma^1\ 2p\pi^{*0})^{14}$, this restriction means that the capture NO^+ can only be formed in the X, b or A states, as formation all other accessible low-lying states of NO^+ require the promotion of a second electron;[40] for these one-electron transitions the $ETF[\mathrm{NO}^{2+}(\mathrm{Y}) \rightarrow \mathrm{NO}^{+}(\mathrm{Z})]$ is set to 1/3.

The above discussion explains how the vibrational and electronic transition probabilities for the capture and ejection processes (P_c, P_e) are calculated. In equation (1) P_c and P_e are combined with the Landau-Zener transition probability to give an overall transition probability from a given vibrational level of the ground electronic state of NO^{2+} to a given combination of product vibronic states. The values of *LZP* for each of the transitions to the different combination of product electronic states were calculated using an algorithm which has been described in detail in previous publications.[45] In brief, this algorithm calculates the probability of crossing from the reactant asymptote to the product asymptote by calculating the interspecies separation of the crossing of these potentials. Constructing the simple polarization attraction and Coulomb repulsion potentials used to model the reactant and product PECs[45] requires simply the polarizability of the neutral and the energy separation *S* of reactant and product asymptotes. For the latter quantity, we use the energy gap between the vibrationless levels of the relevant product and reactant electronic states:

$$S = E[\mathrm{NO}^{2+}(\mathrm{X},v^{++}{=}0)] + E[\mathrm{NO}(\mathrm{X},0)] - E[\mathrm{NO}^{+}(Z,v_\mathrm{c}{=}0)] - E[\mathrm{NO}^{+}(Y,v_\mathrm{c}{=}0)]$$

To simulate the experimental ΔE_T spectrum we calculate the values of *P* for all the possible transitions between the bound vibrational states of NO^{2+} and the accessible vibronic states of the NO^+ products, and then weight these transition probabilities using the NO^{2+} vibrational distribution in the ground electronic state of the dication, $N[\mathrm{NO}^{2+}(v^{++})]$. This final weighting is required because, unlike the neutral NO, the reactant NO^{2+} ions will undoubtedly not be in a single vibrational level since they are formed by electron ionization. We estimate $N[\mathrm{NO}^{2+}(v^{++})]$ using FCFs calculated using LEVEL for transitions from the ground vibronic state of NO to the various vibrational levels in the ground electronic state of NO^{2+}.

At the end of this lengthy procedure, we arrive at a list of weighted values of P for all the possible transitions between the bound vibrational states of $NO^{2+}(X)$ and the accessible vibronic states of NO^{+}. For each of these transitions it is straightforward to calculate ΔE_T since the energies of the reactant and product states are known. For the construction of a model ΔE_T spectrum, we form a stick spectrum of these releases with intensities proportional to the appropriate weighted value of P and then convolve with an appropriate Gaussian instrument function to reflect the experimental resolution.

Extra References for Supplementary Information

43. R. J. Le Roy, *Level 7.0*, (2000), University of Waterloo Chemical Physics Research Report CP-58.
44. G. Dawber, A. G. McConkey, L. Avaldi, M. A. MacDonald, G. C. King and R. I. Hall, *Journal of Physics B*, 1994, **27**, 2191.
45. S. A. Rogers, S. D. Price and S. R. Leone, *J. Chem. Phys.*, 1993, **98**, 280.