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Oxygen Abstraction from N_2O with Ground-State Transition Metal Atoms: Density Functional Study on the Mechanism of the Reactions of Sc, Ti, and V + N_2O

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Density functional calculations have been performed on the ground-state, spin-conserving reactions between N_2O and Sc, Ti, and V atom. We have defined a reaction coordinate (N−O bond distance) along which we have investigated the reaction mechanism. Smooth reaction curves and significant exothermicity for each reaction have been obtained. It has been demonstrated that electron transfer from the metal atoms to N_2O is an essential ingredient of the mechanism. This facilitates the bending of the N_2O molecule, the N−O bond weakening, and an $O^-(^2P)$ dissociation without surface crossing. Furthermore via 4s−3d hybridization occurring on the metal atoms the $4s^\beta$ electron is transferred to the dissociating O atom, thus connecting the reactant and product channels without any energy barrier on a single potential energy surface. It has been found that charge transfer from N_2O toward the metal atom compensates the $3d^\alpha$ electron transfer donated by the metal atom, resulting in a net $4s^\beta$ electron transfer. We have found that when the number of 3d electrons equals 3 (in the case of vanadium), the reaction exhibits a mechanism different from the reactions with Sc or Ti, and this can be explained by considering the Pauli repulsion between the interacting orbitals. We have shown that the mechanism predicted in this work is in good accordance with the so-called *electron-transfer* model, whereas only elements of the so-called *direct abstraction* model can be invoked to account for the predicted mechanism.

1. Introduction

Reactions of transition metals with nitrogen oxides and other small oxygen-containing molecules have attracted great attention due to the role these processes play in different fields of chemistry: catalytic activation of the N−O bond, oxidation of transition metals, kinetics of corrosion, and chemistry of the earth's atmosphere (see refs 1−15 and references therein). These reactions can be formulated as Me + OX = MeO + X, where Me stands for the metal atom and X is generally N_2, O, CO, NO, etc. These reactions have been extensively investigated by several groups with different methods, such as beam-gas chemiluminescence, or laser-induced fluorescence techniques. General conclusions have been drawn from analyzing the kinetic data of the oxygen abstraction process from N_2O, O_2, or NO by neutral metal atoms of Sc, Ti, or V. Three different mechanisms have been proposed to account for the observed features of the kinetics: the general inefficiency of the reactions (small preexponentials in the kinetic equations which indicate that a large fraction of the collisions is elastic) and the less than 2−4 kcal/mol activation energies.

In the surface-crossing model[9,10] (also called the direct abstraction mechanism[3]) it is assumed that a neutral O atom is transferred to the metal atom, and the electronic state of the metal atom is important. The ground state of the Sc, Ti, or V can be written as $4s^23d^n$, where $n = 1$, 2, and 3, respectively. The lowest electronic configurations of the MeO reaction products however correlate asymptotically with the lowest excited $4s^13d^{n+1}$ atomic states. Thus, the reaction path should go over the barrier where the $4s^23d^n$ and the $4s^13d^{n+1}$ surfaces cross. According to this model, the order of the reaction rates with a given OX molecule can be estimated by considering the excitation energies of the metal atoms, which suggests the $k_{Sc} < k_{Ti} < k_V$ order. This however does not agree with the experimentally measured order ($k_{Ti} < k_V < k_{Sc}$).[10] On the other hand, this mechanism can explain the increased reactivity of the excited-state atoms.[15]

The electron-transfer (ET) mechanism is another model that has been frequently invoked to explain the kinetic data of the Me + N_2O reactions.[9,10] This mechanism is a modification of the so-called harpoon mechanism.[16] According to the ET mechanism, at a certain distance the potential energy surface responsible for the interaction of the ground-state neutral reactants crosses the surface corresponding to the interaction of the $Me^+ + OX^-$ ion pair. This means that when the reactants approach each other, at the crossing point an electron transfer occurs. The reaction then takes place on the ionic surface and the MeO formation is completed by an O^- abstraction to Me^+. The crossing point can be estimated from the metal ionization energy and the electron affinity of the OX molecule. In addition, for a given OX molecule, the order of the reaction rates can be predicted by comparing the metal ionization energies, and also for a given metal, the electron affinities of the OX molecules determine the order of rates within this model. For the Me + N_2O reactions, this model correctly predicts the rate order $k_{Ti} < k_V < k_{Sc}$.[10] Moreover, this model can explain the increased reactivity of the excited metal atoms: the ionization energy of an excited atom is smaller than that of the ground-state atom; the crossing of the neutral and ion-pair surfaces occurs in farther regions, which means a more efficient reaction. Nevertheless the model gives incorrect orders when we consider the reactions of a certain metal atom with different OX molecules.[10,14]

The third method was introduced by Futerko and Fontijn[11−13] and is called the resonance interaction model. In this model

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the Arrhenius parameters and rate constants are estimated by taking into account the ionization potential, the s−p excitation energies of the metal atoms, the electron affinity of N_2O, and the bond energy in the MeO molecule. It has been shown that although for main group metals it performs well, the model does not correctly predict the properties of the reactions of transition metals, mainly due to the fact that it neglects the metal d electrons and the electronic structure of the product MeO.[4−7]

In our study we have performed density functional calculations in order to determine ground-state reaction paths for the Me + N_2O interactions, where M is Sc, Ti, or V. Knowledge about the electronic structure of the reaction intermediates can be very important for understanding and explaining chemical reactivities and reaction routes. Our purposes hence were (a) to characterize efficient reaction paths and locate significant points on the potential energy surfaces; (b) to analyze the electronic changes during the reactions and determine the reaction mechanism; and (c) to compare the derived mechanism with those deduced from the experiments.

2. Computational Details

The density functional calculations have been performed with the deMon program package[17] within the LCGTO-DF formalism.[18] The Becke88 nonlocal exchange[19] and the Perdew86 nonlocal correlation[20] gradient corrections were added to the Vosko−Wilk−Nusair local type exchange−correlation functional[21] throughout the calculations. The orbitals were expanded using a 9s/6p/1d Gaussian basis for N and O and 15s/9p/5d basis for the transition metal atoms. The contraction pattern was (5211/411/1) for N and O, while for the metal atoms the contraction pattern was (63321/5211/41). Uncontracted auxiliary basis sets were used to fit the charge densities and the exchange−correlation potential. Their patterns were (10,5,5) for the metal atoms and (7,5,2) for the nitrogen and oxygen atoms. The basis set superposition error (BSSE) was estimated in several stages of the reactions. It was found that this error is always smaller than 3 kcal/mol. Although fluctuations within this value cannot be predicted correctly, the steepness of the reaction curves indicates that energy barriers are likely not masked by BSSE alone. The grid for the numerical integration of the exchange−correlation terms had 64 radial points and 50, 110, or 194 angular points, depending on the distance from the nucleus. The algorithm following the reaction coordinate was the steepest descent method. We set the threshold of the maximum atomic displacement to 0.02 au, providing in this way that the optimization can effectively scan the fine details of the potential energy surface.

3. Results

3.1. Overall Features of the Reactions. We have assumed that there are two main reaction paths for the reactions: one is when the metal atom approaches the N−O bond from a "side-on" direction, the other route is when the arrangement of the four atoms is close to a collinear ("end-on") geometry. To model the oxygen abstraction from the "side-on" direction, we placed the metal atoms at a distance of 2.5 Å from both the oxygen and the N atoms of the N−O bond and allowed the systems to relax. Figures 1, 2, and 3 represent the calculated reaction curves along with the most important geometrical arrangements. Since we found that the N−O bond length increased monotonically as the optimization proceeded, we chose the N−O bond distance as the independent variable and we plotted the total energy with respect to this variable. In all three cases the geometry optimizations yielded smooth curves without any energy barrier, producing N_2 and MeO. We note that we cannot exclude the possibility that there is a barrier on these curves, but its height should be within 3−5 kcal/mol due to the error sources of our methodology. At the end of the optimizations we found that the two products formed a weak N_2−MeO complex. Table 1 shows the energy values obtained for the reactions. It can be seen that the order of the exothermicity is Ti > V > Sc, irrespective of whether we take into account the extra stabilization caused by the final complex formation. The calculated reaction energies are in good agreement with the experimental reaction enthalpies in the case

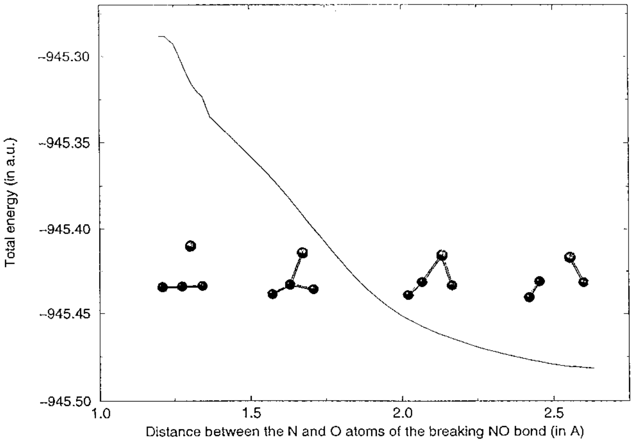

Figure 1. Reaction energy curve for the $Sc(4s^23d^1) + N_2O(^1\Sigma^+)$ reaction.

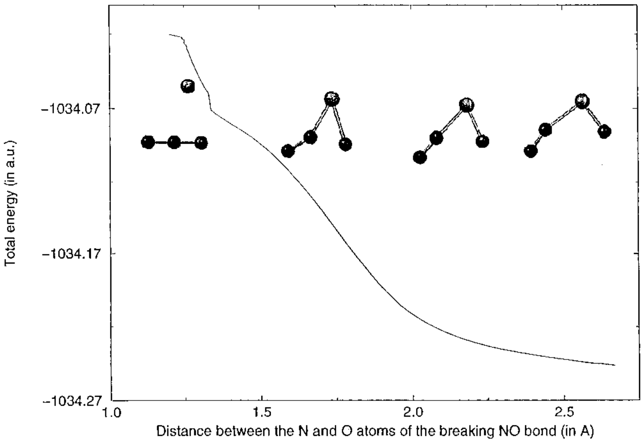

Figure 2. Reaction energy curve for the $Ti(4s^23d^2) + N_2O(^1\Sigma^+)$ reaction.

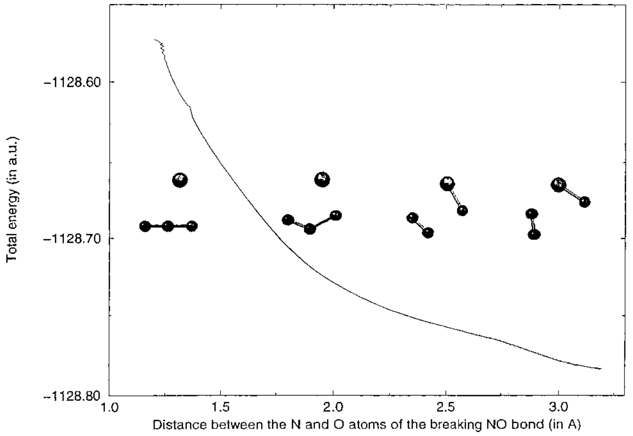

Figure 3. Reaction energy curve for the $V(4s^23d^3) + N_2O(^1\Sigma^+)$ reaction.

TABLE 1: Reaction Energies and Stabilities of the Final Products (in kcal/mol)

metal atom	reaction energy[a,b]	reaction energy[c]	stability of the final complex
Sc	107.7 (126 ± 4)	112.9	5.2
Ti	117.8 (121 ± 3)	131.0	13.2
V	112.4 (113 ± 7)	122.0	9.6

[a] Calculated as the difference between the energy of the isolated products and the initial reagents; atomic energies are calculated using nonspherical electron densities and integral numbers for occupying the atomic orbitals. [b] The experimental ΔH°_{298} values are in parentheses (from ref 10). [c] Estimated from the height of the reaction curves; the reaction energies calculated in this way involve the extra energy from the final complex formation.

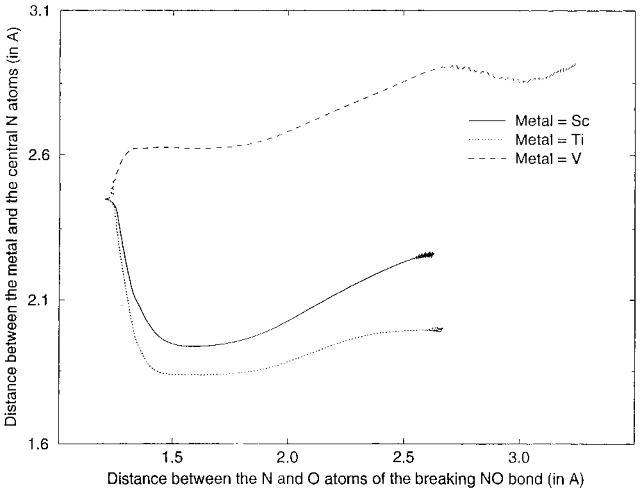

Figure 4. Metal-central nitrogen distance curves for the reactions.

of Ti and V, while for Sc we predicted a slightly underestimated value. Comparison of the atomic rearrangements of the three reactions reveals a striking difference between the reaction of V and those of the other two metals: although in all cases the bending of N_2O is a very typical and essential step, when the metal atom is V, the central N atom of N_2O tilts away from the metal atom, whereas in the other two cases it bends toward the metal atom. In Figure 4 the Me−N distances are plotted against the reaction coordinate. This figure clearly shows the different deformation of N_2O for V compared to Sc and Ti. The consequence of the differing motion is that complex formation takes place between the V atom and the terminal N atom of the N_2O molecule, whereas in the other two cases the MeO molecule interacts with the N_2 molecule via the N atom participating in the breaking of the N−O link. Apart from this fact, the forms of the reaction curves are very similar. It is interesting to note that a similar reaction curve was obtained for the Ti + CO_2 reaction.[22] The similarity can be explained by the fact that CO_2 and N_2O are isoelectronic and their electron structures are analogous. We have also performed calculations on the reactions taking place from an "end-on" initial arrangement (with a metal−oxygen distance of 2.5 Å) and found the following: Sc and Ti can abstract an O atom from N_2O from this initial structure, whereas V cannot; in each case we had to displace the atoms of N_2O from the perfect collinear arrangement, tilting the molecule slightly in order to avoid getting trapped at the saddle point; the reactions required many more optimization steps to proceed; final complex formations did not occur due to the initial arrangement (the metal atom cannot interact with the N_2 molecule). It suggests that the direction of the approaching metal atom plays an important role in the reaction efficiency. Therefore the experimentally observed inefficiency of these reactions can be related to the fact that a large number of resultless (elastic) collisions take place with not only the inert N_2 part of an N_2O molecule but also the more reactive N−O part from unsuited directions. Thus from here on we focus our discussion on the reaction path started from the "side-on" arrangements in order to elucidate the mechanism of the effective channel.

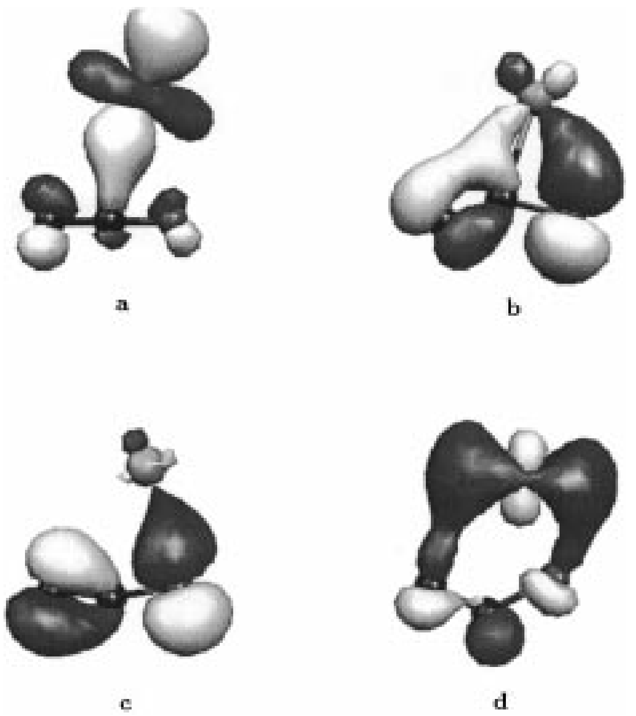

Figure 5. a) Charge transfer from the metal atom toward the in-plane LUMO (3π) of N_2O. (b) Charge transfer from the in-plane HOMO (2π) of N_2O to the metal atom. (c) Orbital interaction responsible for the different atomic motion in the V + N_2O reaction (d) Charge transfer from the V atom to the in-plane LUMO (3π) of N_2O via 4s-3d hybrid.

3.2. Reaction Mechanism. Analyzing the orbitals revealed the following mechanism for the reaction of Sc and Ti. A charge transfer with α spin (spin up) occurs at the initial stage of the reaction from the metal atom to the in-plane LUMO of N_2O (3π), which has anti-bonding character for both the N−O and the N−N bonds (see Figure 5a). Population of this orbital however bends the molecule, because the optimal state of the N_2O^- ion is bent (with destabilized N−O and N−N bonds).[23] In addition, formation of a bent N_2O^- ion is a favorable process, as shown by the experimental electron affinity: 5.07 kcal/mol[23] (for the sign see ref 24). On the other hand, the vertical electron affinity of N_2O is −51.42 kcal/mol (this value was obtained by combining experimental and MCSCF/CI results[23]). We have also estimated theoretically these electron affinity values and obtained 0.48 kcal/mol for the adiabatic and −25.99 kcal/mol for the vertical processes. It is obvious that the trend is the same for the experimental and theoretical affinities, although the theoretical values do not agree with the experimental ones (due to the fact that our methodology was not designed for such calculation: further basis set improvement and ZPVE corrections would be necessary). The trend discussed here clearly shows that the N_2O molecule cannot keep its linear structure when its LUMO is populated. This charge transfer will form one of the 3π orbitals of the metal oxide. As the reaction further proceeds, the in-plane HOMO of N_2O (2π) starts to populate an empty metal d orbital allowed by symmetry (Figure 5b). This charge transfer is responsible for the formation of the metal oxide 8σ orbital. At the same time another charge transfer starts from a 4s−3d hybrid orbital of β spin (spin down) toward the

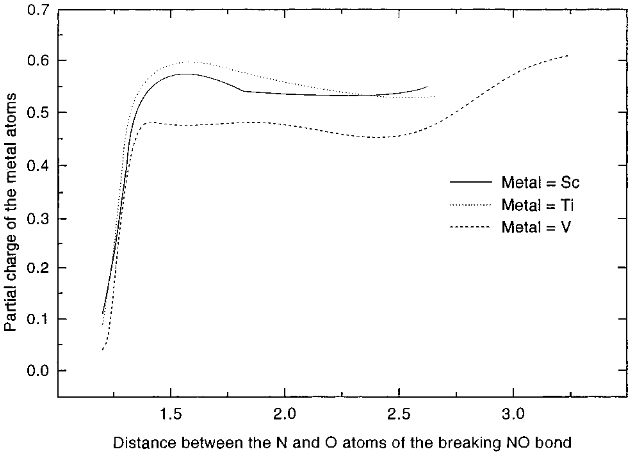

Figure 6. Partial charge of the metal atoms during the reactions.

3π orbital of N_2O. Due to this charge transfer the $4s^{\beta}$ orbital quickly becomes empty. Rolling down on the potential energy surface, the N—O bond is further destabilized, then breaks because of the formation of the new Me—O molecule. By contrast, the N—N bond starts to strengthen again. After the N—O bond breaks, the N_2 and the MeO formation is completed and the two reaction products form a weak complex, giving rise to a small additional stabilization of the system.

When the reagent metal atom is vanadium, at the initial stage of the reaction the previously described $d_{metal} \rightarrow 3\pi_{N_2O}$ charge transfer occurs. However, charge back-donation from N_2O to the metal d orbital is unfavorable, because this orbital is occupied by an electron (Pauli repulsion). The other empty d orbitals are not available for this overlap because of their symmetry. Hence the N_2O molecule tilts away from the metal atom (Figure 5c). This motion certainly counteracts the initial $d_{metal} \rightarrow 3\pi_{N_2O}$ charge transfer. Instead, the vanadium atom interacts with the $3\pi_{N_2O}$ orbital for both α and β spins via 4s—3d hybrids, which are however mainly composed of the 4s metal orbital (Figure 5d). In this way, both the N—N and N—O bonds weaken. In the following stages, the N_2 part starts to shift away from the O atom, which allows the Me—O bond formation. Careful inspection of the orbitals revealed that the $4s^{\alpha}$ electron of vanadium was not transferred to the N_2O molecule, while the $4s^{\beta}$ orbital was already empty in a quite early period of the reaction. It is seen from the structures of Figure 3 that in the final weak complex the N_2 is bonded to the MeO via the terminal N atom through which the charge donation from V occurred.

To emphasize the importance of charge transfer, we plotted the partial charges of the reacting metal atoms with respect to the reaction coordinate in Figure 6. As it is seen all three metal atoms become strongly positive at the beginning of the reactions and then slowly stabilize around 0.55—0.60*e*. The initial jump of the three curves indicates similar electronic processes at the early stages of the reactions. On the other hand the slightly different curve for V shows that this metal can stabilize its partial charge in a later stage of the reaction due to the different mechanism. This stage corresponds to the region of the potential energy surface where the distance between the N_2 and V—O fragments is the largest during the reaction. As the reaction further proceeds, the stronger interaction with the N_2 molecule increases the partial charge of V.

3.3. Discussion of the Mechanisms. In this section we examine the electronic reorganization and its roles in detail. When analyzing reaction mechanisms from an electronic point of view, we have to consider two important factors: spins and occupation of atomic orbitals.[25] It can be easily seen that the postulate of spin conservation bears a close relation to the problems raised by the direct abstraction model (crossing of surfaces resulting from electronic states having different spin). On the other hand, the electron-transfer mechanism requires thorough orbital considerations. There are two essential problems often emphasized in connection with the reaction between transition metals and N_2O, and both problems correspond basically to the question of spin conservation:

(i) The diabatic (spin-conserving) dissociation of N_2O

$$N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_g^{\ +}) + O(^1D)$$

produces an unreactive, excited-state oxygen atom, well above the adiabatic $N_2(^1\Sigma_g{}^1) + O(^3P)$ surface. This has been considered as a severe constraint in the Me + N_2O reactions,[6,9,10] because the $O(^1D)$ state correlates with the high-energy MeO states, whereas the MeO ground and low-energy states correlate to the $O(^3P)$ atomic state. It has been therefore assumed that a hopping from the $O(^1D)$ surface to the $O(^3P)$ surface is partly responsible for the slow reaction rate.

(ii) The atomic asymptote of the transition metal atoms in the low-lying states of the MeO reaction product is $4s^13d^{n+1}$ instead of the ground state $4s^23d^n$ configuration. As discussed in the Introduction, this controversy stimulated the development of the surface-crossing mechanism.

Our calculation revealed that the initial electron transfer from the metal atom toward the N_2O molecule yields a N_2O^- ion (Mulliken population analysis indicated ca. 0.5*e* transferred to N_2O, and the bending of the molecule also shows this fact). The dissociation of a bent N_2O^- however follows this spin-conserving route:

$$N_2O(^2A') \rightarrow N_2(^1\Sigma_g^{\ +}) + O^-(^2P)$$

The bond between the metal and oxygen atoms in all three MeO molecules can be represented as a transition between the ionic and covalent bond, due to the large electronegativity of oxygen and the large charge separation in the molecules.[26] In this sense the ground state of the ScO, TiO, and VO correlates with the ionic $Me^+(4s^13d^n) + O^-(^2P)$ states; consequently the dissociation of N_2O^- can be connected to the MeO formation without any surface crossing. This fact underlines the importance of the charge transfer during the reaction: in this way the dissociation of N_2O is directly coupled to the Me^+O^- formation without barrier coming from surface crossings.

The initial charge transfer is an essential, integral part of the mechanism. To demonstrate this, we present Figure 7, where the potential energy curves describing the interaction of a linear N_2O molecule and ($4s^23d^n$) and ($4s^13d^{n+1}$) metal atoms are depicted. The geometry of N_2O was fixed at the equilibrium geometry (d(NN) = 1.150 Å, d(NO) = 1.200 Å), and the distance between the metal atom and the center of the N—O bond was varied. Due to the linearity of N_2O, no charge transfer can occur from the metals to the N_2O LUMO, because the vertical electronegativity of N_2O is highly negative. As is clearly seen from the graphs, the interactions of both the ground state and the excited-state metal atoms with the linear N_2O are repulsive, except for the $Sc(4s^13d^2)$ case, where the curve is slightly attractive with −8.8 kcal/mol depth. From the behavior of the curves we can deduce that neither the ground state nor the excited state of the metal atoms can interact with the N_2O without charge transfer. This observation strongly supports the ET model, namely, that charge transfer is an indispensable element of the mechanism. In addition, Figure 7 demonstrates

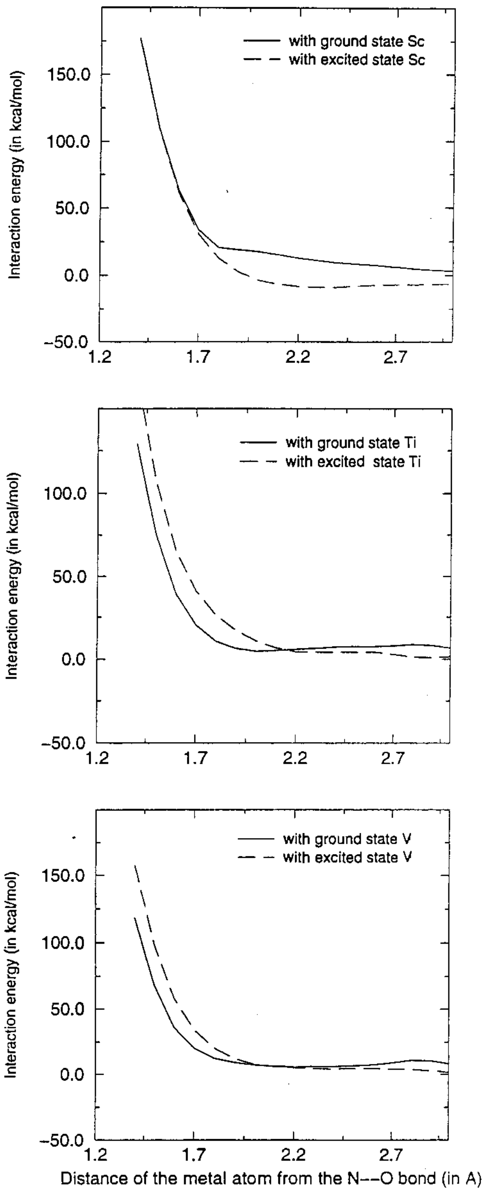

Figure 7. Interaction curves of ground- and excited-state Sc, Ti, and V atoms with a linear N_2O molecule.

that the excited, but neutral Sc, Ti, or V atoms are not reactive enough to interact with the N−O bond, which indicates that the pure direct abstraction mechanism (without taking into account charge flow) cannot be applied for these reactions.

Although both the adiabatic dissociation of neutral N_2O and the adiabatic MeO formation involve crossing of surfaces evolving from different spin states, the complete reaction is not spin-forbidden:

$$N_2O(^1\Sigma^+) + {}^{2S+1=n+1}Me \rightarrow N_2(^1\Sigma_g^+) + {}^{2S+1=n+1}MeO$$

As we have shown, the dissociation of N_2O^- takes place on a single potential energy surface; therefore it follows that the MeO formation with $O^-(^2P)$ anion coming from N_2O^- should also take place without jumping to another surface. The smooth energy curves strongly indicate such processes. Closer inspection of the electronic orbitals in different stages of the reactions however revealed that small excitations should occur because 4s−3d hybridization has an important role during the reaction. Let us investigate the metal oxide formation by taking the reaction of Ti as an example. Ground-state TiO has an electron configuration of $7\sigma^2 8\sigma^2 3\pi^4 9\sigma^1 1\delta^1$ (considering only the levels deriving from the valence atomic orbitals). The two highest orbitals are almost solely composed of the metal 4s and 3d orbitals, respectively, and the configuration correlates with the excited neutral Ti($4s^1 3d^3$) and ionic Ti^+($4s^1 3d^2$) states. It follows therefore that the $4s^\beta$ electron of the metal atom should be transferred to the N_2O molecule during the reaction. It is important to see that the same charge transfer can be predicted from the lowest ionization process of Ti (or the other two metals): Ti($4s^2 3d^2$) → Ti^+($4s^1 3d^2$) + e^-. It is seen that the characteristic feature is the loss of the $4s^\beta$ electron for all three metals. This scheme (simple $4s^\beta$ electron transfer from the metal atom toward the N_2O molecule) would be completely in accordance with the ET mechanism. However the calculation clearly demonstrated that at first charge transfer occurs from the $3d^\alpha$ orbitals because of their more favorable orientations and symmetry properties. This process corresponds to a higher ionization process. In the following steps 4s−3d hybridization occurs and the charge transfers are taking place via these hybrid orbitals for both α and β spins. Formation of the hybrid orbitals is facilitated by the continuously decreasing local symmetry around the metal atom. Nonetheless the back-donation from N_2O to the metal 3d orbitals compensates the initial loss of d^α electrons, whereas the $4s^\beta$ electron is irreversibly transferred to the N_2O molecule (and later exclusively to the O atom) via the 4s−3d hybrid. Since 4s−3d hybridization means a certain degree of excitation, we can expect that this process introduces an energy barrier in the reaction curve. The fact that this energy barrier is overcompensated by the formation of the new bonds in our calculation (as the smooth energy curves show) can probably be associated with the tendency of the DF methodology to overstabilize the configurations where electrons are on the *n*d orbitals instead of the more diffuse (*n*+1)s orbital.[27,28] It follows that the energies required for the 4s−3d hybridization occurring in each reaction are underestimated. It is however difficult to estimate the degree of excitation involved in the hybridization; consequently the estimation of the introduced error is complicated. We speculate that this error can be a few (3−5) kcal/mol in energy, which (together with BSSE) however can effectively mask reaction barriers having heights within this region. On the other hand, we do not expect that the overall mechanism would be influenced by this error. As for the V atom, the somewhat different atomic motions do not change substantially the foregoing mechanism: apart from the initial 3d → 3π electron transfer, the 4s−3d hybrids play a role in the charge donations. The difference between the mechanisms is that the p orbital of the middle nitrogen atom does not participate in the orbital-overlapping processes owing to the direction of N_2O bending.

In summary the mechanism governing the oxygen abstraction from N_2O by Sc, Ti, or V has two important ingredients: (i) electron transfer from the metals to the N_2O molecule via initially 3d, then 4s−3d hybrid orbitals, which promotes the N−O bond weakening and the O^- dissociation without surface crossing; (ii) electron transfer from N_2O toward the metal atom which compensates the initial α charge transfer, yielding a net $4s^\beta$ electron loss of the metals. This orbital interaction is also responsible for the different motion of N_2O during the reaction with V.

According to our calculations, the ET model serves as a useful scheme to explain the N−O cleavage, where the direct abstraction model in its original form cannot be applied. However elements of this model (excitation and its role in the charge transfer due to the hybridization) are necessary to complete the

ET mechanism. We also found that the collinear arrangement is not suitable for the effective charge transfers. The orbital overlaps in this geometry are not efficient to bend the N_2O molecule, which is a prerequisite for the reaction. Thus we conclude that the "side-on" initial arrangement is the favorable structure for the reaction, while the collinear approach is not effective for the oxygen abstraction, and this fact plays an important role in the low efficiency of the reactions.

4. Summary

From the calculations the following conclusions emerged: Oxygen abstraction reactions of N_2O by Sc, Ti, and V are smooth, spin-conserving processes having less than ca. 5 kcal/mol activation energies, in agreement with experiments.[9,10] Electron transfer from the metal atom to N_2O is very important because in this way the N−O bond weakens and an $O^-(^2P)$ can dissociate without surface crossing. Charge back-donation from N_2O toward the metal atom in the later stages of the reaction has a crucial role in how the N_2O molecule tilts during the Me−O formation. 4s−3d hybridization takes place on the metal atom, which facilitates the $4s^\beta$ electron transfer to the N_2O molecule. Breaking of the N−O bond and the formation of MeO product do not require surface crossing, whereas the hybridization during the electron transfers involves excitation. It was also demonstrated that these reactions cannot take place without electron transfer either on the ground or the first excited potential energy surfaces. From the results we proposed that the "side-on" collisions are more effective than the collinear approaches. Although we tried to make a comparison between our results and experimental findings, it has to be kept in mind that the dynamics of the reactions is completely left out of account. Rate constants basically reflect the average of many efficient and inefficient collisions, but we restricted ourselves to consider efficient reaction routes; therefore predictions concerning the kinetics of the reactions can hardly be made. The motion of the reacting molecules and atoms certainly gives rise to effects that cannot be described in our methodology. Instead we focused on the microscopical processes not seen experimentally. We speculate that if a suitable arrangement is formed by the thermal motions of the reacting atoms (very few events from all collisions), the orbital reorganizations controlling the reactions are essentially not effected by the temperature. On the other hand, the final complex formation obtained by the calculations is the consequence of neglecting the thermal motions. Nevertheless the vibrational motions of N_2O even facilitate the reactions. Especially shift along the bending normal mode increases the electron affinity of N_2O, assisting in this way the charge donations from the metal atom.

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