

molecular orbital is located on the methine carbon-hydrogen bond (41%).

Indeed, this molecular orbital has little metal character (4% of the total electron density is concentrated in the cobalt $d_{x^2-y^2}$ orbital). The oxygen atoms contain 12% of the electron density in p_x orbitals and only 6% in the oxygen lone pairs (p_y orbitals). The benzene rings account for a further 29% of the total electron density in the HOMO with all of it concentrated in the C-H linkages closest to the methine C-H bond. Thus, the reductant is drawn into a cavity of electron density (70% of the total in this molecular orbital) in the region of the methine carbon to form the precursor complex.

The energy for the HOMO of the $[\text{Co}(\text{en})_2(\text{dppd})]^{2+}$ complex is $-1066 \text{ kJ mol}^{-1}$ and that of the $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$ complex is very similar at $-1127 \text{ kJ mol}^{-1}$. The rate constant for the reduction of $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$ by $\text{Cr}(\text{II})$ is exceedingly slow ($5.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 50°C).³⁵ The corresponding reduction of $[\text{Co}(\text{en})_2(\text{dppd})]^{2+}$ is characterized by a complex mechanism, but the rate is at least 8000 times faster than that of $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$. Thus, two such very different rates with orbitals of so similar energy suggests that the mechanism of reduction must be quite different for the two compounds.

It appears from this study that there are no obvious structural differences that could account for the striking dissimilarities in the redox properties exhibited by the two closely related β -diketone complexes. The molecular orbital calculations indicate that the position of attack of the reductant to form a precursor complex is determined by the location of the maximum electron density in the HOMO. Usually, that would be expected to lie on the lone pairs of the coordinating oxygen atoms but in the case of the dppd complex, the strongly electron-withdrawing nature of the benzene rings shifts this density onto the central carbon atom. Further structural and molecular orbital studies are in progress to determine if these observations are general features of inner-sphere redox processes.

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Registry No. $[\text{Co}(\text{en})_2(\text{dppd})](\text{ClO}_4)_2$, 113774-77-9; $[\text{Co}(\text{en})_2(\text{N}_3)_2](\text{ClO}_4)_2$, 14877-87-3; $[\text{Cr}(\text{OH}_2)_5(\text{dppd})]^+$, 113705-88-7; $[\text{Cr}(\text{OH}_2)_6]^{2+}$, 20574-26-9; $[\text{Co}(\text{en})_2(\text{dppd})](\text{NO}_3)_2$, 113774-78-0; $[\text{Co}(\text{en})_2(\text{ptdn})]^{2+}$, 33570-80-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom parameters (2 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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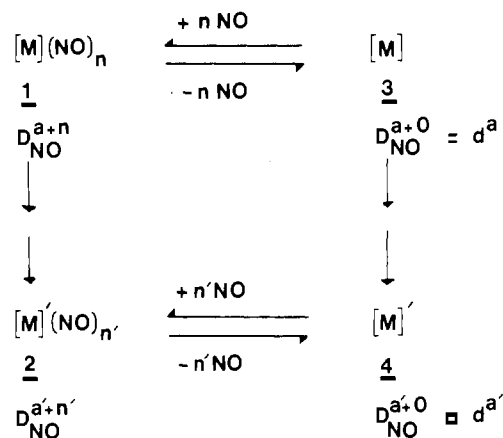
A Notation for Describing Redox Processes in the Surface Chemistry of Nitrosyl Complexes

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It is common to describe the reactions of nitric oxide with metallic centers on oxides or in zeolites in terms of an oxidation or a reduction of the metallic element. Unfortunately, this is not devoid of ambiguities in view of the amphoteric nature of the NO ligand.¹ For example, formation of a mononitrosyl cobalt from

Scheme I



the reaction of NO gas with a Co^{2+} -exchanged zeolite A has been interpreted either as no redox change² or as an oxidation.³ On Co^{2+} -exchanged zeolite Y, reaction with NO to yield a surface dinitrosyl has been regarded either as a reduction⁴ of the Co or as a redox-inactive process.^{2,5} On the other hand, we recently reported the formation of a similar dinitrosyl species following the deposition of $\text{Co}(\text{CO})_3\text{NO}$ on either Al_2O_3 or zeolite Y,⁷ but we described the reactions in terms of an oxidation of the cobalt sites.

We propose a shorthand notation for specifying the type of metallic centers present in NO complexes that should remove any ambiguity as to what the terms oxidation and reduction refer during reactions with nitrosylated species, whether they occur under heterogeneous or homogeneous conditions.⁸ This notation becomes equivalent to the familiar d^a notation of the formal electronic configuration of the metal in a nonnitrosylated transition-metal complex.⁹

Notation

Any $[\text{M}](\text{NO})_n$ complex can always be constructed in a formal way by the complexation of n NO molecules on the center $[\text{M}]$ where the square brackets stand for an unspecified set of non-nitrosyl ligands. If the electron configuration of the metal in the NO-free species $[\text{M}]$ is d^a , then the same metal center in the $[\text{M}](\text{NO})_n$ complex can be represented as being of type $\text{D}_{\text{NO}}^{a+n}$. In this notation, a is the number of d electrons in $[\text{M}]$ left by the dissociation (D) of the n NO ligands removed in the molecular form. In addition, according to the notation of Enemark and Feltham,¹⁰ if the complex type of $[\text{M}](\text{NO})_n$ is $\{\text{M}(\text{NO})_n\}^b$, then one has $b = a + n$ and the complex type can be rewritten as $\{\text{M}(\text{NO})_n\}^{a+n}$, as suggested previously by us,⁷ which contains the same information as the $\text{D}_{\text{NO}}^{a+n}$ notation except that the structural parameter n (the number of NO ligands) is not repeated. Note that for the NO-free species $[\text{M}]$ the metallic center becomes of

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type D_{NO}^{a+0} , which is equivalent to the d^a notation. As an example, $Co(NO)_3$ is a $\{M(NO)_3\}^{12}$ complex that contains a D_{NO}^{9+3} cobalt. As shown by the notation, this complex could in principle result from the addition of three NO molecules on one D_{NO}^{9+0} (d^9) $Co(0)$ center.

Any conversion (Scheme I) of a D_{NO}^{a+n} $[M](NO)_n$ complex **1** into a $D_{NO}^{a+n'}$ $[M'](NO)_{n'}$ complex **2** can then be achieved according to two pathways. The first one involves the actual set of reactions required to obtain **2** from **1**. The second formal pathway involves the NO-free progenitors **3** and **4** of species **1** and **2**, respectively, in which the metallic center is of type D_{NO}^{a+0} for **3** and of type $D_{NO}^{a'+0}$ for **4**. By this route the redox changes that accompany the conversion of **1** into **2** can be broken down into two components. The first type pertains to the complexation-decomplexation steps interconverting **1** with **3** and **2** with **4**, whereas the second type involves the NO-free species **3** and **4**. Redox changes of the first type pertain exclusively to the transfer of electrons between the metal and NO occurring upon the formation of covalent MNO linkages. Depending on the results of electron bookkeeping, based on the $NO^+ - NO^-$ dichotomy,^{1b,11} the complexation-decomplexation steps can result in a formal oxidation, or a reduction, or no redox change at M. However, these redox processes can be viewed as temporary, with the NO ligands acting merely as electron pumps.^{1c,8a} For example, complexation of n NO ligands on **3** to yield **1** followed by decomplexation of the n NO molecules restores the initial electronic configuration of $[M]$. According to our proposed notation, it is readily seen that such temporary redox changes leave invariant the electronic parameter a in D_{NO}^{a+n} and that only the structural parameter n is altered. It is only during processes like the conversion of **3** into **4** that the parameter a is modified and such changes can be labeled as nontemporary. Once the D_{NO}^{a+n} type of metal centers involved is specified, it is immediately clear what type of redox process has to be considered.

Examples

The reaction of NO with Co^{2+} -exchanged zeolites that initially contained a $Co(II)$ center, (i.e. of type D_{NO}^{7+0}) yielded $[Co](NO)_n$ species that, according to the published discussions, should contain in every case a cobalt of type D_{NO}^{7+n} ($n = 1$ for zeolite A,^{2,3} $n = 1$ or 2 for zeolite Y^{2,4,5}). Therefore, the redox changes were exclusively of the temporary type. Whether they can be best described as an oxidation, a reduction, or no redox change at the metal depends upon what formal ligand type (NO^- , NO^+ , or neutral NO) is chosen. Diverging opinions can then be anticipated, and this is indeed what is found.

Alternatively, in the reaction of $Co(CO)_3NO$ (a D_{NO}^{9+1} cobalt) with Al_2O_3 ⁶ or zeolite Y,⁷ the formation of D_{NO}^{7+2} species must necessarily involve a nontemporary two-electron oxidation of cobalt, and this was the only change we considered in discussing the results. However, there are no existing guidelines that could have restricted us from discussing this transformation in terms of the overall contribution of the temporary and nontemporary changes. Then, depending upon which one of the descriptions of these D_{NO}^{7+2} species proposed in the literature^{2,4,5} is favored, the net result of the reactions could have been presented as either a one- or three-electron oxidation of the metal.¹³ As soon as the D_{NO}^{a+n} notation is used, such potentially confusing situations cease to exist.

Other examples of the interaction of NO with surface sites that appear to be of the complexation-decomplexation type can be

Table I. Examples of Reactions Involving NO Complexes in Relation to the D_{NO}^{a+n} Notation

R1	$Co(CO)_3NO$ D_{NO}^{9+1}	\xrightarrow{NO}	$Co(NO)_3$ D_{NO}^{9+3}		Ref. 24.
R2	$Cr(CO)_6$ D_{NO}^{6+0}	$\xrightarrow{h\nu}$	$Cr(NO)_4$ D_{NO}^{6+4}		Ref. 25.
R3	$[CpCr(CO)_3]_2$ $[D_{NO}^{5+0}]_2$	\xrightarrow{NO}	$CpCr(CO)_2NO$ D_{NO}^{5+1}	$[Cp = \eta^5-C_5H_5]$	Ref. 26.
R4	$CpV(CO)_3CN$ D_{NO}^{4+0}	\xrightarrow{NO}	$CpV(NO)_2CO$ D_{NO}^{4+2}		Ref. 27.
R5	$[W(O-tBu)_3]_2$ $[D_{NO}^{3+0}]_2$	$\xrightarrow{NO, py}$	$W(O-tBu)_3(NO)(py)$ D_{NO}^{3+1}	$py = \text{pyridine}$	Ref. 28.
R6	$(Cp)_2Ni$ D_{NO}^{8+0}	\xrightarrow{NO}	$CpNi(NO)$ D_{NO}^{9+1}		Ref. 29. (see text).
R7	$2 Co(NCS)_2L_3(NO)^+$ $2 D_{NO}^{7+1}$	\longrightarrow	$Co(NO)_2L_2^+ + Co(NCS)_2L_4^+$ $D_{NO}^{8+2} \quad D_{NO}^{6+0}$		Ref. 21. (see text).

found with Fe^{2+} -exchanged zeolite Y.^{14,15} One D_{NO}^{6+1} iron species with a $\nu(NO)$ at 1778 cm^{-1} was formulated¹⁵ as $[Fe^I(NO)]^{2+}$, implying a temporary one-electron reduction of the metal. However, in order to assign a specific number of electrons to a temporary change, one must know the coordination mode of the NO. The NO stretching frequency has often been used for this, but it can be quite unreliable.^{1a,8a,16}

Even when structural data are available, the interpretation of the results can remain equivocal. For the mononitrosyl formed on Co^{2+} zeolite A, in one instance³ XPS data were considered to be consistent with the X-ray diffraction results leading to the formulation of the species as $[Co^{III}(NO)]^{2+}$, whereas the same XPS data were interpreted by others² as favoring a $[Co^{II}(NO)]^{2+}$ formulation. Describing this species as a $\{M(NO)\}^8$ [or $\{M(NO)\}^{7+1}$] complex containing a D_{NO}^{7+1} cobalt avoids the difficulties and the ambiguities of assigning a formal oxidation state to the metal.

Finally, the notation proposed is also straightforward to apply for nitrosyl complexes under homogeneous conditions. The reaction of NO gas with $CoXL_4^+$ ($X = \text{halogen}$, $L = \text{phosphite}$) containing a D_{NO}^{8+0} (d^7) cobalt to yield a D_{NO}^{8+1} $CoXL_3(NO)^+$ derivative¹⁸ is a simple NO for L substitution leaving the electronic parameter a unchanged. The redox processes that might affect the metal are, therefore, exclusively of the temporary type. The same conclusion applies to R1–R5 as additional examples. (See Table I.) Alternatively, the formation of the dimer $(Co(NO)_2Cl)_2$ (each Co is D_{NO}^{8+0}) from a reaction between $CoCl_2$ [D_{NO}^{8+0}] and NO in a basic alcoholic medium is an example of a nontemporary reduction with the concomitant formation of alkyl nitrites as oxidation products.¹⁹ Similarly, a nontemporary reduction of the metallic center occurs in the reaction of nickelocene (Cp_2Ni) with NO to yield $CpNiNO$ in R6. A final example is the conversion²⁰ of $Co(NCS)_2(L)_2(NO)$ ($L = \text{PMe}_3$) into $Co(NO)_2(L)_2^+$ and $Co(NCS)_3(L)_2$, which is closely related to the transformation²¹

- (11) When the MNO angle of the covalent MNO linkage is less than about 140° , the NO coordination mode is classified as bent and the NO ligand is treated formally as NO^- , and when the MNO angle falls in the approximate range $180-155^\circ$, the coordination mode is classified as linear and NO is regarded formally as NO^+ (see ref 22 for examples). For reviews of the structures of NO complexes see ref 12.
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of $\text{Co}(\text{NCS})(\text{L}')_3\text{NO}^+$ [$\text{L}' = \text{P}(\text{OEt})_3, \text{PPh}(\text{OEt})_2$] into an equimolar mixture of $\text{Co}(\text{NO})_2(\text{L}')_2^+$ and $\text{Co}(\text{NCS})_2(\text{L}')_4^+$ (see R7). In both cases a dismutation is occurring, but whether the cobalt in the cationic dinitrosyl product is regarded formally as $\text{Co}(-\text{I})$, as in ref 20, or as $\text{Co}(\text{I})$, as in ref 21, is irrelevant to this conclusion. In each case, one deals with a $\text{D}_{\text{NO}}^{8+2}$ dinitrosyl formed concomitantly with a $\text{D}_{\text{NO}}^{6+0}$ species starting from a $\text{D}_{\text{NO}}^{7+1}$ complex. That a nontemporary dismutation is indeed involved is seen at once when one considers the variation of the parameter a .

In conclusion, lack of recognition of the types of redox processes possible in the chemistry of NO complexes can obscure the nature of the reactions involved. This is particularly of concern in studies of surfaces where direct information on the state of a catalytically active surface acquired by using NO^{23} as a probe molecule can

only be obtained when it can be shown that the electronic parameter a remains invariant during nitrosylation. We believe that the notation proposed will help to clarify the description of the chemistry in allowing a self-explanatory identification of the redox processes that can be discussed.

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Additions and Corrections

1986, Volume 25

M. M. Taqui Khan* and V. Vijay Sen Reddy: New Terdentate Ligands Containing Nitrogen and Phosphorus or Arsenic as Donor Atoms and Their Complexes with Ruthenium(II) and -(III).

Page 212. Lines 6–9 should read as follows: The three triplets centered at 58.92, 53.70, and 35.24 ppm are assigned to phosphorus atoms P_A , P_B , and P_C (structure III) with a $J(\text{P}-\text{P})$ coupling constant of 24 Hz. A $J(\text{P}-\text{P})$ value of 24 Hz is typical....—V. Vijay Sen Reddy