Exploring the Potential Energy Surface of the Association of Cu^+ to Oxaziridine, Nitrosomethane, and Formaldoxime

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Received: June 29, 1998; In Final Form: September 22, 1998

The catalytic role of Cu^+ on the isomerization processes among oxaziridine and its isomers methylenimine *N*-oxide, nitrosomethane, and formaldoxime has been investigated by studying the corresponding potential energy surfaces through the use of high-level DFT calculations. The geometries of the different stationary points were optimized at the B3LYP/6-311G(d,p) level while the final energies were obtained using a 6-311+G-(2df,2p) basis set expansion. Our results show that oxaziridine, contrary to what has been found for formamide, behaves as a nitrogen base when the reference acid is Cu^+, since the oxygen-attached species is predicted to be 9.2 kcal/mol less stable than the nitrogen-attached structure. Both nitrosomethane and formaldoxime are also predicted to be nitrogen bases in gas-phase reactions with Cu^+, while for methylenimine *N*-oxide only the oxygen and the carbon-attached complexes were found to be minima of the potential energy surface, the former being almost 21 kcal/mol more stable than the latter. Among the cationized species the most stable corresponds to the attachment of the metal cation to the nitrogen atom of formaldoxime, which is also the most stable neutral. However, the energy gaps found for the neutral species differ significantly from those found for the corresponding Cu^+ complexes. Cu^+ association to oxaziridine catalyzes the C−O bond fission, favoring the formation of an open $H_2C-NH-OCu^+$ complex. The isomerization processes leading from nitrosomethane to formaldoxime and to methylenimine *N*-oxide as well as that connecting the latter two compounds are also catalyzed by Cu^+ association in the gas phase.

Introduction

The cationization of neutral molecules by association with metal cations is one of the most important topics in ion chemistry in the gas phase.[1] Very often metal cation association is accompanied by significant bond activation effects, which lead to spontaneous unimolecular fragmentations or favor collision-induced dissociation processes.[1] On the other hand, the metallic complexation of some organic molecules is relevant from the biological point of view to understand the biochemical mechanisms governing the cation exchanges at the cellular level. These kinds of reactions often involve transition-metal cations, which can play an important role in the catalysis of some processes. In particular, considerable effort has been devoted recently to investigate the interactions between Cu^+ and molecules of biochemical interest as α-amino acids,[2,3] since Cu^+ reactions play an important role in biological media.[4,5] However, a complete knowledge of the gas-phase reactivity of these systems requires a reliable description of the corresponding potential energy surfaces (PESs), which is normally attained through the use of ab initio molecular orbital techniques. Unfortunately, the size of molecules of biological interest is so large that their theoretical treatment at high ab initio levels becomes computationally unaffordable. Hence, in the past few years we have considered it of interest, as a good alternative, to model these big molecules by smaller systems that present similar active sites within similar environments. This prompted us to investigate the gas-phase reactions of guanidine[6] and formamide[7] with Cu^+ and to analyze the possible catalytic role[8] that this metal monocation can play in isomerization processes involving formamide.

The aim of this paper is to study the most outstanding features of the PES of complexes between Cu^+ and oxaziridine, which can be viewed as the cyclic isomer of formamide. Oxaziridines were first described by Emmons in 1957.[9a] Ever since, this kind of compound has received a much attention from the mechanistic and structural points of view. It presents a rich rearrangement chemistry,[9b] and some of their derivatives can be used as oxygen-transfer or epoxidation agents in olefines, sulfides, enolates, and other compounds.[9c,d] Oxaziridines possess a nitrogen stereogenic center, which is of interest for synthesis purposes.[9e] Quite often, cyclic systems present a gas-phase reactivity significantly different from that of the corresponding open-chain analogues. The differences in the intrinsic basicities of saturated[10,11] and unsaturated[12] lactones with respect to the corresponding open-chain aliphatic esters are paradigmatic examples of these cyclization effects. Whether similar cyclization effects appear in oxaziridine when the reference acid is a metal monocation as Cu^+ is one of the objectives of our study. Oxaziridine can be seen as a model for the epoxidation of imino groups which are very relevant in biological systems. It is a well-known phenomenon that the opening of such kind of cycles may play an important role in carcinogenic processes. Another

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10.1021/jp982796i CCC: $15.00

point of interest is to investigate whether Cu^+ association stabilizes oxaziridine with respect to formamide, for which a complete survey of the PES of its association with Cu^+ has been recently reported in the literature.[7] In fact, it has been shown[13] that protonation and Li^+ association stabilizes three-membered rings, in particular when they have some antiaromatic character or present several basic centers.

Although oxaziridine **1** itself has not been isolated yet and was only detected as an intermediate in some reaction mechanisms, it can isomerize to other stable species as nitrosomethane ($H_3C{-}NO$, **2)** and formaldoxime ($H_2C{-}NOH$, **3)** as well as into methylimine *N*-oxide ($H_2C{-}NH{-}O$, **4)**. A theoretical study[14] on the isomerization processes involving **2**, **3**, and **4** has been recently reported in the literature. The aim of this paper is to investigate the possible catalytic role of Cu^+ association on the oxaziridine → methylimine *N*-oxide → nitrosomethane → formaldoxime isomerizations, as well as the evaluation of the gas-phase Cu^+ binding energies. For this purpose we need to include in our theoretical treatment all the possible isomerization processes including oxaziridine which were not included in previous studies.

Computational Details

Standard density functional theory (DFT) calculations have been carried out using the Gaussian-94 series of programs.[15] Among the different DFT approaches available in this program package we have chosen the hybrid density functional B3LYP method,[16] which has been shown to not only yield reliable geometries and vibrational frequencies for a great variety of systems[17] but also provide Cu^+ binding energies in fairly good agreement both with experimental values, when available, and with high-level ab initio calculations.[18] It should be mentioned that B3LYP approach has been shown[14] to yield reliable structures for the particular set of neutral compounds included in this study. This DFT approach combines Becke's three-parameter, nonlocal hybrid exchange potential[16] with the nonlocal correlation functional of Lee, Yang, and Parr.[19]

The geometries of the different species under consideration have been optimized by using the all-electron (14s9p5d/9s5p3d) basis of Watchers−Hay[20] for Cu, supplemented with one set of f polarization function and the 6-311G(d,p) basis set for the remaining atoms of the system. The harmonic vibrational frequencies of the different stationary points of the PES have been calculated at the same level of theory in order to classify the stationary points of the PES as local minima or transition states (TS) and to estimate the corresponding zero-point energies.

We have previously shown,[18] for a test set of small molecules, that the association energies for Cu^+ complexes obtained at the DFT/6-311+G(2df,2p) level are in reasonably good agreement with those estimated in the framework of the G2 theory,[21] where a 6-311+G(3df,2p) basis is the largest basis set expansion used. Hence, the same approach will be used in this study. It must be noted that, for the sake of simplicity, we keep the nomenclature 6-311+G(2df,2p) for all the atoms of the complex, although for Cu^+ the basis set used corresponds to the (14s9p5d/9s5p3d) Watchers−Hay's basis supplemented with a set of (1s2p1d) diffuse components and with two sets of f functions (rather than d functions) and one set of g functions (rather than f functions) as polarization basis. On the other hand, it should also be taken into account that the basis set employed in these DFT calculations differs from that used in the G2 formalism in the number of sets of d (f for Cu) polarization functions included on the heavy atoms. We have shown[18] for some smaller Cu^+ complexes that the binding energies so obtained do not differ significantly from those calculated with the larger basis set, while the computation time decreases considerably.

As we have mentioned in the Introduction, metal cation association usually implies bond activation effects which may lead to or favor bond fission. The detection of these activation effects requires a good knowledge of the bonding characteristics of the complexes under consideration. For this purpose we have used the atoms in molecules (AIM) theory of Bader,[22] which is based on a topological analysis of both the electron density function, $\rho(\mathbf{r})$, and its Laplacian, $\nabla^2\rho(\mathbf{r})$. The values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at the bond critical points (i.e., points where is minimum along the bond path and maximum in the other two directions) give useful information regarding the strength of the linkages. Actually, the Laplacian of the density identifies regions of the space wherein the electronic charge is locally depleted ($\nabla^2\rho(\mathbf{r}) > 0$) or concentrated ($\nabla^2\rho(\mathbf{r}) < 0$). The former situation is typically associated with interactions between closed-shell systems (ionic bonds, hydrogen bonds, and van der Waals molecules), while the latter characterizes covalent bonds. There are however significant exceptions, mainly when the atoms involved in the bond are very electronegative. In these cases the so-called energy density, $H(\mathbf{r})$, is a more reliable index.[23] In general, a stabilizing charge concentration in the bonding region, a situation which is typically associated with covalent bonds, is characterized by a negative value of the energy density, so the interactions between the different atoms of the complex can be unambiguously classified. The AIM analysis was performed using the AIMPAC series of programs.[24]

To also gain additional insight into changes in the character of the lone pairs of the bases, due to the isomerization processes that take place along the different reaction paths, we have also used the natural bond orbital (NBO) analysis of Weinhold et al.,[25] which usually yields reliable atomic charges and provides a chemical description of the bonding in terms of interactions between atomic hybrids.

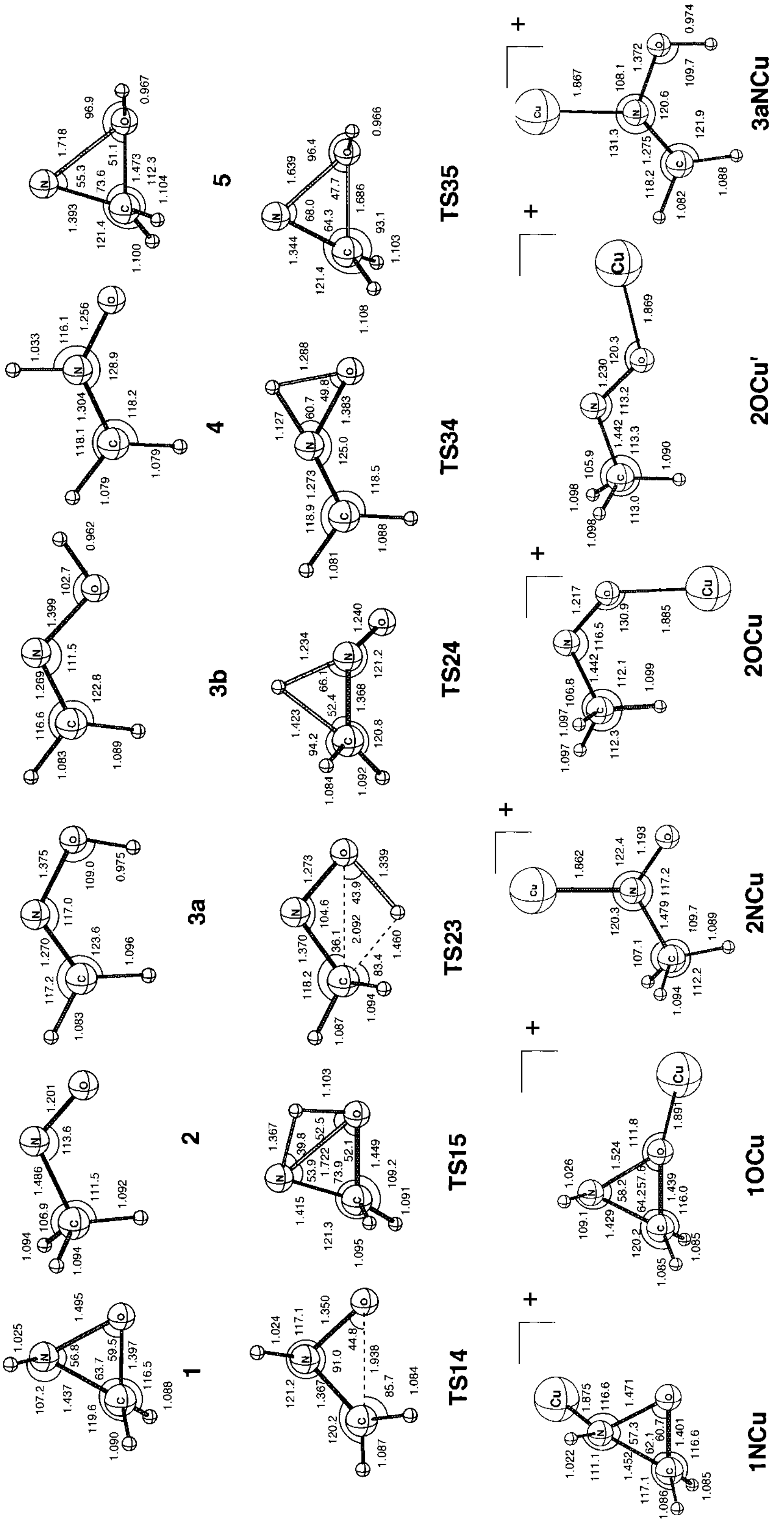
Results and Discussion

In our theoretical survey we have optimized the geometries of all the possible conformers of each species, because, as we shall see later, in some cases not only the most stable conformer is involved in the different isomerization processes. For similar reasons we have also considered the attachment of Cu^+ to all possible basic centers of the different neutrals.

The B3LYP/6-311G(d,p) optimized geometries are given in Figure 1. This figure also includes the optimized geometries of the transient species involved in the isomerizations between the different neutral and cationic local minima. Their total energies are summarized in Table 1.

The complexes so formed are identified, indicating the number which designates the neutral followed by the basic center to which the Cu^+ is attached. For instance, Cu^+ association to the oxygen atom of oxaziridine (**1**) would yield complex **1OCu**, while the attachment to the nitrogen would yield complex **1NCu**. The same nomenclature was adopted to designate the different transition states. In this case two digits are used to identify the two local minima connected by the transition state.

Neutrals. As illustrated in Figure 2, *trans*-formaldoxime (**3b)** is predicted to be the most stable of the species investigated, although it is estimated to be 51.4 kcal/mol less stable than formamide. It is worth noting that this estimate is in very good agreement with the corresponding experimental heats of formation,[26] which differ by 51.0 kcal/mol. Also in nice agreement


1
2
3a
3b
4
5
TS14
TS15
TS23
TS24
TS34
TS35
1NCu
1OCu
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2OCu'
3aNCu
+

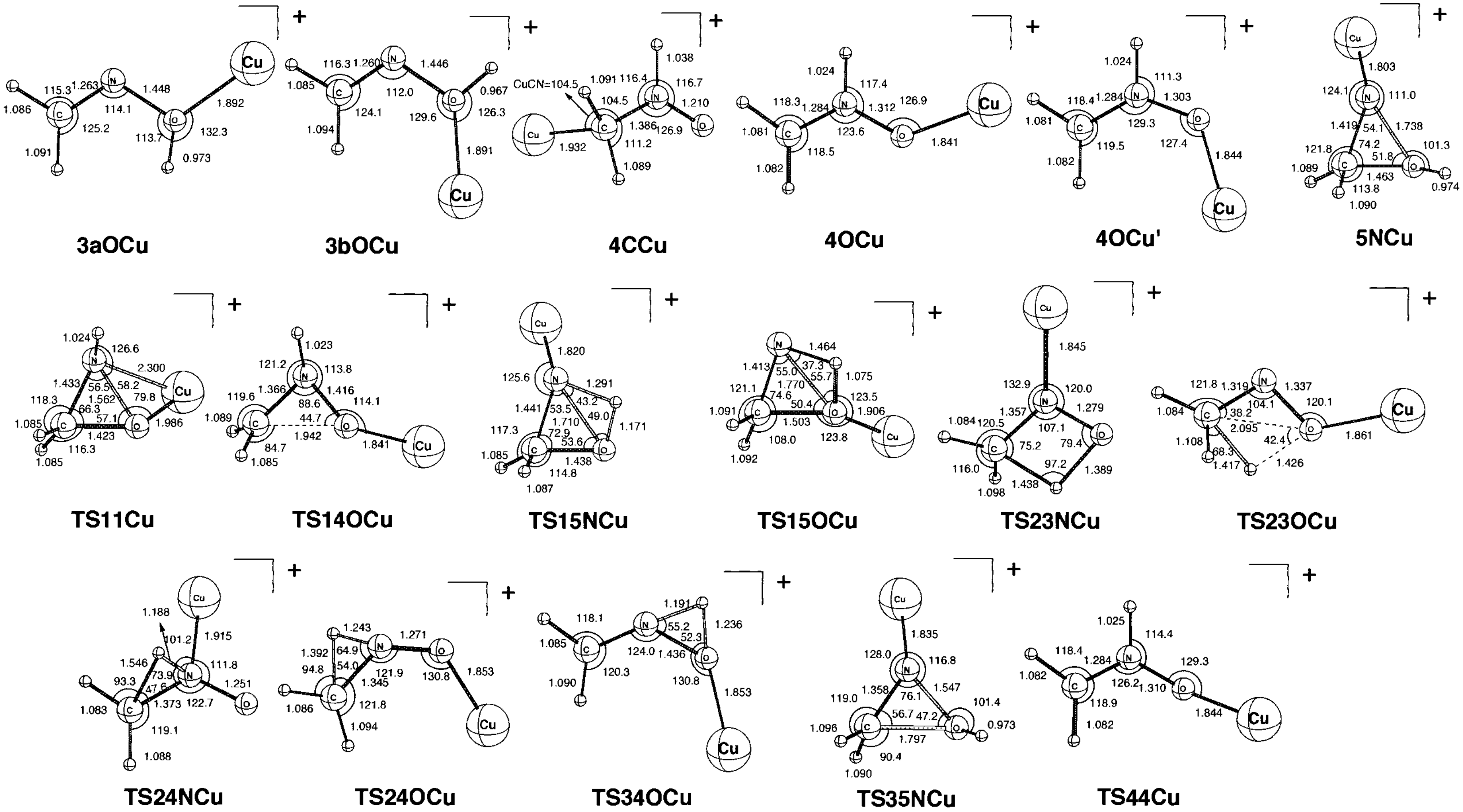


Figure 1. B3LYP/6-311G(d,p) optimized geometries for the different neutrals included in this study and their Cu$^+$ complexes. Bond lengths are in angstroms and bond angles in degrees.

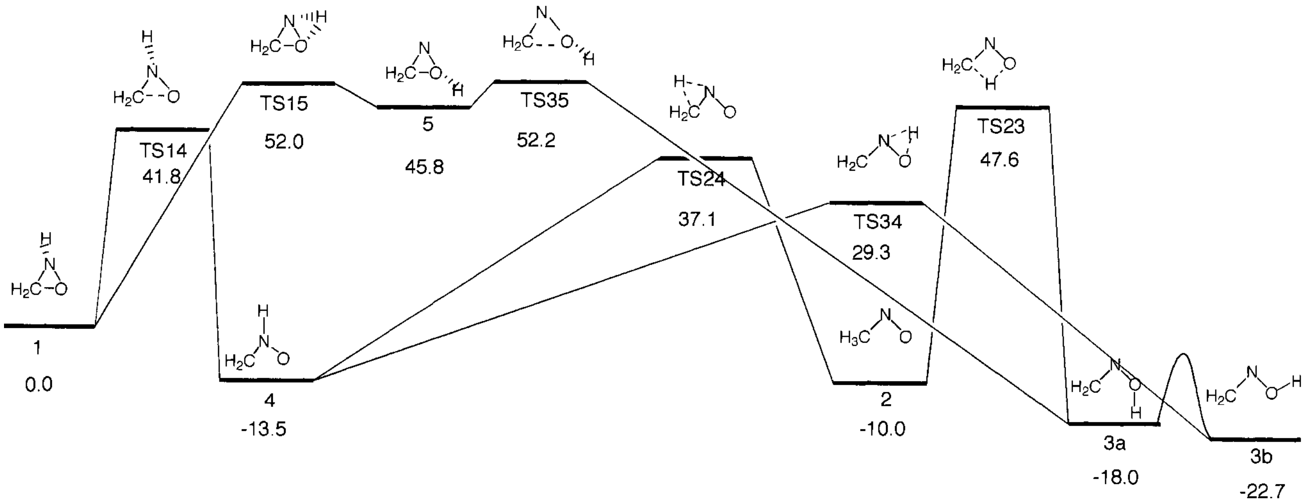


Figure 2. Energy profile of the PES associated with oxaziridine and their isomers included in this study. All values are in kcal/mol.

TABLE 1: B3LYP/6-311+G(2df,2p) Total Energies (*E*), B3LYP/6-311G(d,p) ZPE (hartrees), and Relative Energies (in kcal/mol) for the Different Species under Consideration; Relative Energies Δ*E* (in kcal/mol) Include the Corresponding ZPE Corrections

	E	ZPE	Δ*E*
1	−169.846 49	0.045 51	0.0
2	−169.859 96	0.043 01	−10.0
3a	−169.873 55	0.043 93	−18.0
3b	−169.881 58	0.044 48	−22.7
4	−169.867 54	0.045 08	−13.5
5	−169.771 19	0.043 12	45.8
TS14	−169.776 68	0.042 29	41.8
TS15	−169.757 90	0.039 81	52.0
TS23	−169.762 71	0.037 63	47.6
TS24	−169.780 39	0.038 60	37.1
TS34	−169.792 80	0.038 52	29.3
TS35	−169.759 25	0.041 43	52.2
1OCu	−1810.090 92	0.047 41	0.0
1NCu	−1810.106 27	0.048 13	−9.2
2NCu	−1810.112 16	0.045 73	−14.4
2OCu	−1810.096 57	0.044 47	−5.4
2OCu′	−1810.103 27	0.044 56	−9.5
3aNCu	−1810.138 34	0.046 27	−30.5
3aOCu	−1810.118 85	0.044 63	−19.3
3bOCu	−1810.117 85	0.045 18	−18.3
4CCu	−1810.102 23	0.047 14	−7.3
4OCu	−1810.136 72	0.047 14	−28.9
4OCu′	−1810.135 84	0.047 39	−28.2
5NCu	−1810.059 15	0.046 37	19.3
TS11Cu	−1810.090 39	0.046 69	−0.1
TS14OCu	−1810.041 24	0.044 18	29.1
TS15NCu	−1810.027 43	0.042 26	36.6
TS15OCu	−1809.985 09	0.041 30	62.6
TS23NCu	−1810.013 76	0.039 82	43.7
TS23OCu	−1810.010 23	0.037 92	44.7
TS24NCu	−1810.016 73	0.040 32	42.1
TS24OCu	−1810.043 19	0.040 89	25.9
TS34OCu	−1810.051 04	0.039 62	20.1
TS35NCu	−1810.040 04	0.044 21	29.9
TS44Cu	−1810.135 33	0.046 91	−28.2
1 + Cu	−1810.023 19	0.045 51	41.3

TABLE 2: Calculated Cu^+ Binding Energies (in kcal/mol)

	basic center		
system	N	O	C
1	50.5	41.3	
2	45.7	40.8	
3	49.1	36.9	
4		56.7	35.1
5	67.8		

with the experimental evidence,[26] formaldoxime (**3**) is estimated to be 12.7 kcal/mol more stable than nitrosomethane (**2**). The difference between their experimental heats of formation[26] is 10 ± 0.7 kcal/mol. Hence, we may have confidence in our estimates regarding the relative stability of methylenimine *N*-oxide (**4**) and oxaziridine (**1**), for which no experimental information is available. The predicted stability order is formaldoxime (**3**) > methyleninime *N*-oxide (**4**) > nitrosomethane (**2**) > oxaziridine (**1**). It is important to note that methylenimine *N*-oxide (**4**) is predicted to be 3.5 kcal/mol more stable than nitrosomethane (**2**), though the former has not been experimentally detected. This difference in energy is reduced up to 0.9 kcal/mol at the G2 level of theory.[14] On the other hand, as illustrated in Figure 2, the isomerization barriers that connect the local minimum **4** with other local minima of the PES are quite high, and therefore this species should be experimentally accessible. It can be also observed that a hydrogen transfer from the imino group of oxaziridine toward the oxygen atom yields an intermediate local minimum **5**, which can be viewed as a zwitterionic form of oxaziridine. Although this species lies quite high in energy, it may have some relevance since it is an intermediate in one of the possible oxaziridine → formaldoxime isomerization processes. Moreover, as has been shown previously in the literature,[27] these zwitterionic species are dramatically stabilized by association with metal cations, and they can play an important role in the isomerizations of the corresponding Cu^+ complexes.

Cu^+ Complexes. Our results show that, with the only exception of compounds **4** and **5**, both the oxygen and the nitrogen-attached complexes are local minima of the PES. As can be expected from its zwitterionic character, for compound **5** the oxygen-attached species collapses without activation barrier to **5NCu,** and only the association of Cu^+ to the nitrogen atom was found to be a stationary point of the PES. In contrast, for compound **4**, the nitrogen association is not a favorable process, and the corresponding complex evolves, again without activation barrier, to yield species **4OCu**. We have located, however, a local minimum, **4CCu**, in which the metal cation is associated with the carbon atom of the methylene group, but this structure is more than 20 kcal/mol less stable than the oxygen-attached complex.

The Cu^+ binding energies of the different neutrals have been summarized in Table 2. Similarly to what was found for protonation,[13] oxaziridine (**1**) behaves as a nitrogen base. It is important to recall here that formamide is an oxygen base in the gas phase[7,28] when the reference acids are H^+ or Cu^+.

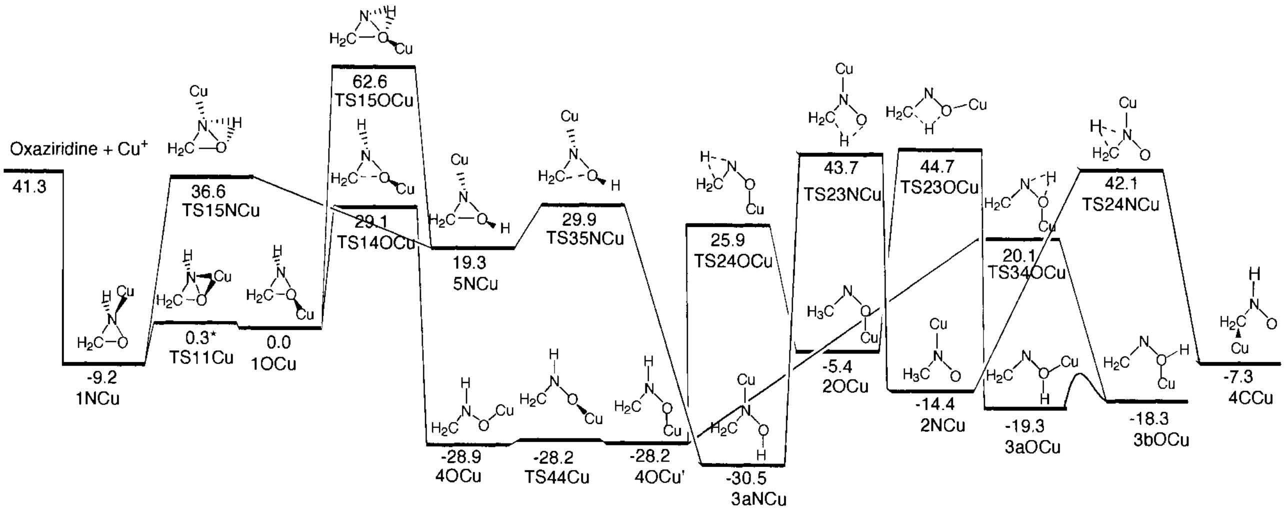


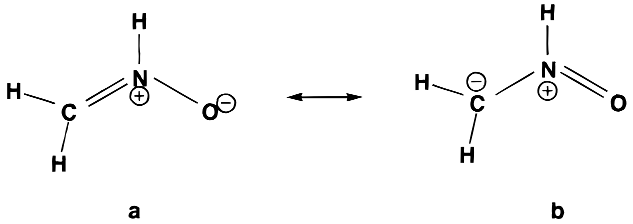
Figure 3. Energy profile of the PES associated with the Cu$^+$ complexes of oxaziridine and their isomers included in this study. Evolution from 2OCU to 3aOCU starts rather from the isomer 2OCu′ ($E_{\mathrm{rel}} = -9.5$ kcal/mol) not included in this figure by simplicity. The value of 0.3 for TS11Cu does not include ZPE. All values are in kcal/mol.

Hence, one must conclude that the cyclization process which leads from formamide to oxaziridine has important effects on the intrinsic basicity of its two basic centers. Actually, our results indicate that the oxygen intrinsic basicity decreases significantly, while the nitrogen intrinsic basicity increases on going from formamide to oxaziridine. A decrease of the oxygen intrisic basicity could be anticipated, taking into account that the oxygen in the C=O group in formamide is more basic than the sp^3 oxygen in oxaziridine (**4**). Besides, in the cyclic form the oxygen atom is bonded to an electronegative NH group, which should result in a decrease of its electron donor ability. The increase in the intrinsic basicity of the nitrogen atom is less obvious and is related to the rehybridization of this basic center, which in three-membered rings is dictated by the size of the ring. The hybrids involved in the N−O and N−C bonds have necessarily a small s character to accommodate a very small bond angle; hence, by orthogonality the hybrid involved in the N−H bond and the lone pair must have a quite large s character. The enhanced electronegativity of the N atom may be satisfied by withdrawing charge from the hydrogen atom. Actually, the NH group becomes more acidic while the nitrogen lone pair becomes more basic, showing the important role of the hydrogen atom of the NH group.[29]

All the remaining species, with the only aforementioned exception of methylenimine *N*-oxide (**4**), which is predicted to be a rather strong oxygen base, behave also as nitrogen bases with respect to Cu$^+$. More importantly, our results show that the Cu$^+$ association energies are quite different for the different species considered. Structures **4** and **5** have the largest Cu$^+$ binding energies due to the high polarity of their N−O bonds. For the particular case of structure **5** this simply reflects its zwitterionic character. Actually, a NBO analysis of the charge distribution of species **5** indicates that an almost unit negative charge is associated with the nitrogen atom. The most important consequence of its enhanced intrinsic basicity is that the energy gap between species **5NCu** and **3aNCu** (49.8 kcal/mol) is significantly smaller than that between the corresponding neutrals (68.7 kcal/mol) (see Figures 2 and 3). Similar findings regarding protonation and Li$^+$ association processes have been reported recently in the literature.[27]

For species **4** the high N$^+$−O$^-$ polarity of its bond indicates that, from the two mesomeric forms that are responsible for its stability (see Scheme 1), form **a** is the main contributor, as reflected by the corresponding NBO analysis. Consistently, the **4NCu** complex, in which the metal cation would be attached to a formal positively charged nitrogen atom, is not a stationary point of the PES as it collapses to the **4OCu** species. The carbon-attached complex **4CCu** is a local minimum, indicating that form **b** also contributes to the stability of compound **4**, although to a lesser degree than form **a**. The most important consequence of the enhanced intrinsic basicity of **4** is that its energy gap with respect to formaldoxime (**3**) is larger than that found between their Cu$^+$ complexes. This means that methylenimine *N*-oxide (**4**) is an oxygen base stronger than formaldoxime (**3**), which is a nitrogen base. As shown in Figure 2, methylenimine *N*-oxide (**4**) can be derived from formaldoxime (**3**) by a 1,2-H shift, through the transient species **TS34**. Hence, on going from **3** to **4** the intrinsic basicity of the oxygen atom should significantly increase, while on going from **4** to **3** the intrinsic basicity of the nitrogen atom should increase. The important point is that the former effect is larger than the latter, due to the strong contribution of the mesomeric form **a** (see Scheme 1). Nevertheless, species **3aNCu** is still the global minimum of the PES (see Figure 3). It must be observed, however, that the formation of this complex implies the internal rotation of the OH group to avoid the repulsion between the positively charged hydrogen atom and Cu. Hence, structure **3aNCu** corresponds to the association of the less stable conformer of formaldoxime.

SCHEME 1



The basicity differences between nitrosomethane (**2**) and formaldoxime (**3**) result in an enlargement of the energy gap between both species upon Cu$^+$ association. These differences can be understood if one takes into account that both forms are connected by a 1,3-H shift. Accordingly, the N=O bond in nitrosomethane is replaced by a C=N double bond in formaldoxime, and this affects the electron donor capacity of the nitrogen atom, since a H_2C=N bond is more easy to polarize

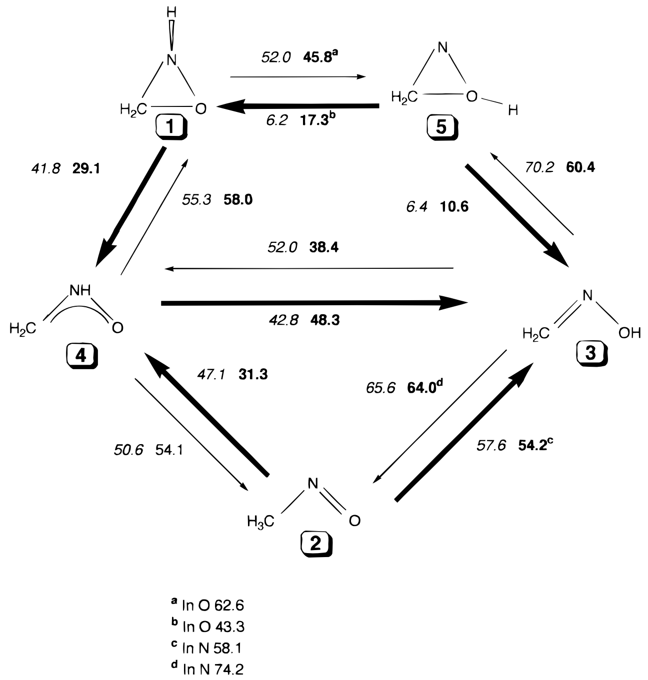


Figure 4. Isomerization barriers, in kcal/mol, between the different neutrals included in this study (*values in italic*) and between their Cu^+ complexes (values in bold). The wide arrows indicate systematically the isomerization process toward the most stable species. The thin arrows correspond to the reverse isomerization processes.

than a N═O linkage. Hence, the lone pair of the nitrogen atom of nitrosomethane should be less basic than that of formaldoxime. This is consistent with the corresponding NBO analysis, which shows that while in the former the s character of the nitrogen lone pair is 29%, in the latter it is only 25%.

In summary, for the Cu^+ complexes the relative stability order is **3aNCu** > **4OCu** > **3aOCu** > **2NCu** > **2OCu′** > **1NCu** > **4CCu** > **2OCu** > **1OCu**.

Catalytic Effects. A comparison between the PESs shown in Figures 2 and 3 clearly shows that the effect of Cu^+ on the isomerization barriers between the different neutrals under consideration is significantly large. For the sake of clarity, we have summarized the values of the different isomerization barriers in Figure 4. In this figure the barriers between the neutrals are indicated in italics while those between the corresponding Cu^+ complexes are written in bold. The wide arrows point always toward the most stable of the two species, while the thin arrows correspond to the reverse process.

It can be seen that **1** → **4**, **2** → **4**, **3** → **4**, **3** → **5**, **5** → **1,** and **2**→ **3** isomerization processes are clearly catalyzed by Cu^+ association, while for the remaining isomerization pathways an increase of the barriers takes place.

The isomerization between oxaziridine (**1**) and methylenimine *N*-oxide (**4**) is catalyzed by Cu^+, because the attachment of the metal cation to the oxygen atom of oxaziridine implies an important activation of the C−O linkage. This is clearly seen when the topological characteristics of the charge density of the neutral are compared with those of the oxygen-attached Cu^+ complex. As illustrated in Table 3, the value of the charge density at the C−O bcp of the complex is sizably smaller than for the neutral. Consistently, the energy density is less negative, indicating a less stabilizing charge concentration within this bonding region. Since the isomerization pathway leading from **1** to **4** implies the fission of the C−O bond, it is reasonable to expect a decrease of the barrier for the corresponding Cu^+ complexes.

TABLE 3: Charge Densities (ρ) and Energy Densities ($H(\mathbf{r})$) of Oxaziridine (1) and Its Oxygen-Attached Cu^+ Complex (1OCu) Evaluated at the Corresponding Bond Critical Point (All Values in au)

	1		1OCu	
	ρ	$H(\mathbf{r})$	ρ	$H(\mathbf{r})$
CN	0.273	−0.304	0.282	−0.331
CO	0.269	−0.359	0.234	−0.291
NO	0.245	−0.169	0.224	−0.144
CuO			0.098	−0.012

The origin of the remaining catalytic effects mentioned above are directly related to changes in the intrinsic basicities of the species involved rather than with bond activation mechanisms. Let us take the **2** → **3** isomerization reaction as a suitable example. As explained above, formaldoxime (**3**) is more basic than nitrosomethane (**2**), and accordingly the transition state connecting both neutrals, namely **TS23**, should exhibit a smaller basicity than **3** but a greater basicity than **2**. Since according to the Hammond postulate the transition state is reactant-like, one should expect a greater stabilization of **TS23** by association with Cu^+ than that undergone by the reactant **2**, leading to a decrease of the corresponding activation barrier between species **2NCu** and **3aNCu**. Entirely similar arguments apply as far as the isomerization processes **2** → **4** and **3** → **4** are concerned.

Conclusions

In agreement with the experimental evidence, our high-level DFT calculations predict formaldoxime (**3**) to be more stable than oxaziridine (**1**) and nitrosomethane (**2**). The methylenimine *N*-oxide isomer (**4**) is also rather stable and should be experimentally accessible, even though it has not been detected yet. Important cyclization effects on the intrinsic basicity of formamide are predicted since, according to our estimates, oxaziridine, contrary to formamide, behaves as a nitrogen base when the reference acid is Cu^+. Actually, the oxygen-attached species is predicted to be 9.2 kcal/mol less stable than the nitrogen-attached structure. Both nitrosomethane and formaldoxime are also predicted to be nitrogen bases when the reference acid is Cu^+, while for methylenimine *N*-oxide only the oxygen and the carbon-attached complexes were found to be minima of the PES, the former being almost 21 kcal/mol more stable than the latter. The most stable Cu^+ corresponds to the attachment of the metal cation to the nitrogen atom of formaldoxime, which is also the most stable neutral. However, Cu^+ association changes significantly the energy gaps between the different neutrals, due to the differences between their intrinsic basicities. Hence, the gap between formaldoxime and methylenimine *N*-oxide is drastically reduced upon Cu^+ association, while that between nitrosomethane and formaldoxime is slightly enlarged. Cu^+ association to the oxygen atom of oxaziridine catalyzes the C−O bond fission, favoring the formation of an open $H_2C{-}NH{-}OCu^+$ complex. The isomerization processes leading from nitrosomethane to formaldoxime and to methylenimine *N*-oxide as well as that connecting the latter two compounds are also catalyzed by Cu^+ association in the gas phase.

Acknowledgment. This work has been partially supported by the DGICYT Project No. PB96-0067 and by the Acción Integrada Hispano-Francesa HF1997-0025. Generous allocations of computational time at the Centro de Computación Científica de la Facultad de Ciencias de la Universidad Autónoma de Madrid and at the Cray-J90 computer of CIEMAT are also acknowledged. A.L. acknowledges a postdoctoral grant from the EC.

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