

orbital. It is evident in Figure 2 that this orbital is significantly elevated when interacted with the diene system including the σ bonds. As a result, the splitting (reflected by the $n \rightarrow \pi^*$ transition) is small enough for the through-space interaction that the through-bond interaction predominates. To our knowledge, this is the only example of a situation in which the through-bond correction actually predominates and exhibits its effect so clearly in the electronic spectra of a molecule.

(13) National Aeronautics and Space Administration Predoctoral Trainee, Sept 1, 1967–Aug 31, 1969.

(14) Supported by Development Award No. 1-K4-GM-42572 from the National Institutes of Health.

Stanley C. Neely,* Robert Fink¹³
Dick van der Helm,¹⁴ Jordan J. Bloomfield

Department of Chemistry, The University of Oklahoma
Norman, Oklahoma 73069

Received February 13, 1971

Bending Nitrosyls in Tetragonal Complexes

Sir:

Nitric oxide coordinates to transition metal ions in either a linear or bent manner.¹ From a structural viewpoint, the linear arrangement has been viewed in terms of NO^+ and the bent arrangement in terms of NO^- , but it seems clear that these bonding descriptions represent too rigid and simplistic a view. As yet, the factors which result in one bonding mode over the other in different nitrosyl complexes have not been fully delineated, although discussions regarding individual systems have appeared.² We have undertaken an examination of nitrosyl bonding in five- and six-coordinate tetragonal complexes, and present herein a correlation of the two bonding modes which allows one to predict which of the arrangements is preferred in a given tetragonal complex.

The procedures employed in this study are similar to those used by Walsh for triatomic systems such as NO_2 and NO_2^+ .³ The two geometries of interest in the five-coordinate tetragonal case are both square-based pyramids, the first possessing a linearly coordinated axial nitrosyl and the second having a bent axial nitrosyl. On the left side of Figure 1, an approximate energy level ordering for the linear nitrosyl complex of C_{4v} symmetry is presented, while on the right side of the figure the energy levels for the bent nitrosyl complex of C_s symmetry are drawn. In correlating the molecular energy levels and orbitals in the two limiting structures, we join only those levels transforming under the same irreducible representation in C_s sym-

(1) For a recent review of nitrosyl complexes, see B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966).

(2) Some representative examples include the following papers: (a) P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, **87**, 3340 (1965); (b) D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.*, 410 (1965); (c) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966); (d) D. J. Hodgson, N. C. Payne, J. A. McGinney, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, **90**, 4486 (1968); (e) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); (f) D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969); (g) D. A. Snyder and D. L. Weaver, *ibid.*, **9**, 2760 (1970); (h) G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1275 (1970); (i) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970); (j) D. M. P. Mingos and J. A. Ibers, *ibid.*, **10**, 1035 (1971); (k) D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *ibid.*, **10**, 1043 (1971); (l) D. M. P. Mingos and J. A. Ibers, *ibid.*, **10**, 1479 (1971).

(3) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

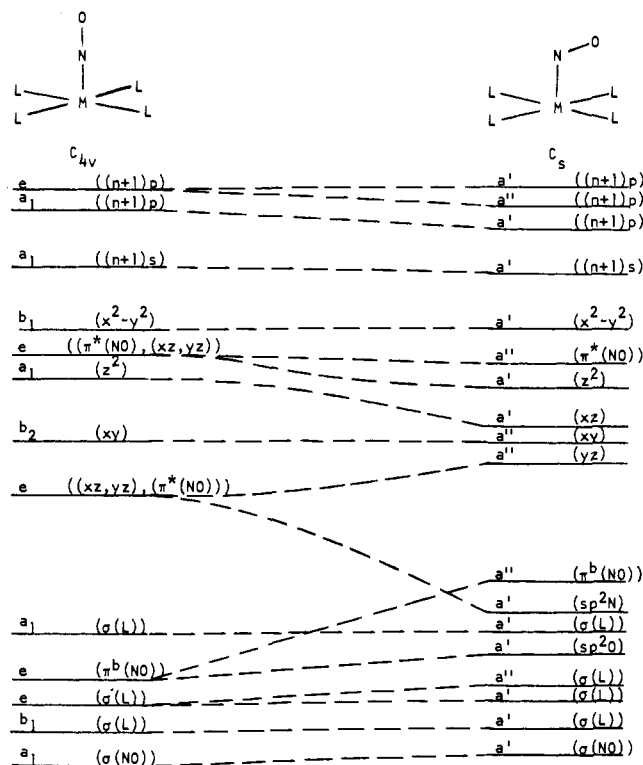


Figure 1. An orbital correlation diagram for the bending of nitrosyls in five-coordinate tetragonal systems. The orientation of the bent nitrosyl group in C_s symmetry is toward one of the basal ligands as has been observed in all of the five-coordinate tetragonal systems with bent nitrosyls studied to date.

metry, and we adhere to the noncrossing rule. Several important correlations are thus found to arise. First, the low-energy doubly degenerate $\pi^b(\text{NO})$ set in C_{4v} symmetry splits as the M–N–O bond angle is changed from 180° , with one member of the set remaining as a $\pi^b(\text{NO})$ function while the other member becomes an oxygen-based nonbonding orbital of a' symmetry. Second, the π -bonding e level delocalized over the metal d_{xz} , d_{yz} orbitals and the nitrosyl $\pi^*(\text{NO})$ functions splits in the reduced symmetry and correlates with the metal d_{yz} (a'') level and the nonbonding orbital of a' symmetry localized on the nitrosyl nitrogen atom. This latter correlation is of fundamental significance, since it is precisely the change in orbital character from a primarily metal-based π function to one localized on the nitrosyl group which explains the oxidative-addition process in the coordination of NO^+ to certain d^8 metal ions.⁴ A third correlation is that of the d_{z^2} level in C_{4v} symmetry, which is σ^* with respect to the metal–nitrosyl bond, correlating with the largely nonbonding d_{z^2} (a') level in C_s symmetry. Lastly, the higher energy $\pi^* e$ level splits and correlates with the $a'' \pi^*(\text{NO})$ level and the metal-based a' level denoted as d_{z^2} .

The correlation diagram thus implies that for a 20-electron system composed of 10 electrons in the ligand σ^b functions, 4 electrons in the $\pi^b(\text{NO})$ set, and a d^6 metal ion, the C_{4v} configuration in which strong $\text{M} \rightarrow \text{NO} \pi$ bonding exists is the geometry of the ground

(4) In this regard, we note that the delocalized π -bonding e level in C_{4v} symmetry is traditionally assigned to the metal d_{xz} , d_{yz} set, thus leading to the NO^+ formulation for the nitrosyl, regardless of the per cent of metal character calculated for the molecular orbitals belonging to this level.

Table I. Number of Electrons and Bonding Mode in Tetragonal Nitrosyl Complexes (L = P(C₆H₅)₃)

| | No. of e ⁻ 's | M-N-O angle, deg | $\nu(\text{NO})$, cm ⁻¹ |
|---|--------------------------|------------------|-------------------------------------|
| Five-Coordinate Systems | | | |
| Fe(NO)(S ₂ CN(CH ₃) ₂) ₂ ^a | 21 | 170.4 (6) | |
| Fe(NO)(S ₂ C ₂ (CN) ₂) ₂ ²⁻ b | 21 | 168 | 1645 |
| Ir(NO)Cl(CO)L ₂ ⁺ c | 22 | 124 (1) | 1680 |
| Ir(NO)I(CO)L ₂ ⁺ d | 22 | 125 (3) | 1720 |
| Ru(NO) ₂ ClL ₂ ⁺ e | 22 | 136 (1) | 1687 |
| Ir(NO)Cl ₂ L ₂ ^f | 22 | 123 (2) | 1560 |
| Six-Coordinate Systems | | | |
| Co(NO)(en) ₂ Cl ⁺ g | 24 | 121 (1) | 1611 |
| Co(NO)(NH ₃) ₅ ²⁺ h | 24 | 119 (1) | 1610 |
| Fe(NO)(CN) ₅ ²⁻ i | 22 | 178 (1) | 1939 |
| Mn(NO)(CN) ₅ ³⁻ j | 22 | 173 | 1725 |
| Cr(NO)(CN) ₅ ³⁻ i | 21 | 176 (1) | 1645 |
| Ru(NO)(OH)(NO) ₂ ²⁻ k | 22 | 180 (5) | 1907 |
| Five-Coordinate Trigonal-Bipyramidal Systems | | | |
| Ir(NO)HL ₃ ⁺ l | 22 | 175 (3) | 1715 |
| Ru(NO)HL ₃ ^m | 22 | 176 (1) | 1640 |
| Ru(NO)(diphos) ₂ ⁺ m | 22 | 174 (1) | 1673 |

^a See ref 2g. ^b See ref 6. ^c See ref 2d. ^d See ref 2e. ^e See ref 5. ^f See ref 2i. ^g See ref 2f. ^h C. S. Pratt, B. A. Coyle, and J. A. Ibers, American Crystallographic Association Abstracts, Summer Meeting, 1971, Ottawa, Canada, Abstract No. C8; C. S. Pratt and J. A. Ibers, quoted in ref 1. ⁱ See ref 2a and P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963). ^j A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, 1180 (1966); J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970). ^k S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, **27**, 309 (1965). ^l See ref 2k. ^m C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3050 (1971).

state. If additional electrons are then added to the system, however, the nitrosyl bends and the molecule undergoes an electron shift from metal to ligand. The placement of electrons in a significantly antibonding orbital in C_{4v} symmetry is thus avoided at the energetic expense of significant metal-nitrosyl π bonding. We conclude that a 22-electron system possessing a tetragonal-pyramidal structure should therefore exhibit a bent nitrosyl coordination, and this is indeed the case.^{2d,e,i,j,5} In Table I, various structurally known nitrosyl complexes are tabulated along with the number of electrons and the nitrosyl bonding mode for each system. The five-coordinate Fe complexes in Table I are 21-electron systems, and they exhibit intermediate structures with slightly bent nitrosyl groups.^{2g,6} There are as yet no structural examples of pentacoordinate nitrosyl complexes having C_{4v} symmetry, presumably because of the ready availability of the open coordination site and the π acidity of the linearly coordinated nitrosyl.

The addition of a sixth ligand trans to NO requires only minor modifications in the correlation diagram. In each geometry, there is the addition of another ligand-based σ^b level and a change in the ordering of the ligand-field levels as a result of the raising in energy of d_{z²}. The resultant ordering in C_{4v} symmetry is probably a₁(z²) > b₁(x² - y²) > e(($\pi^*(\text{NO})$), (xy), yz)) > . . . , as proposed by Manoharan and Gray,^{2a,c} while the corresponding ordering in C_s symmetry is suggested as a'(x² - y²) > a'(z²) > a'($\pi^*(\text{NO})$) > a'(xz) >⁷

(5) C. G. Pierpont, D. G. VanDerveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4760 (1970).

(6) I. M. Rae, *Chem. Commun.*, 1245 (1967).

In correlating the levels of the two six-coordinate geometries, the only substantive changes from the five-coordinate case presented in Figure 1 are that the a' component of the π^* e level now joins with the largely nonbonding a'(xz) level in C_s symmetry and that the a₁(z²) level correlates with one of the a' levels which is strongly σ^* in character. We find, however, that the correlations involving the two more stable π -bonding e levels remain relatively unchanged and, hence, our conclusions are similar to those given above for the tetragonal-pyramidal systems with the addition of one σ^b level. Thus, the complexes Mn(CN)₅(NO)³⁻ (a 22-electron system) and Cr(CN)₅(NO)³⁻ (a 21-electron system) can be expected to have linear NO's, while the complexes Co(en)₂Cl(NO)⁺ and Co(NH₃)₅(NO)²⁺ (24-electron systems) can be expected to possess bent configurations despite the very comparable values of $\nu(\text{NO})$ in these complexes. These expectations are borne out by the structural results.^{2f,8,9}

Two important conclusions emerge from these considerations. First, it is the "antibondedness" of the level to be filled in C_{4v} symmetry, and not its composition, which leads to the distortion from the tetragonal symmetry and the bending of the nitrosyl group. Second, $\nu(\text{NO})$ is not a good structural diagnostic for the mode of nitrosyl coordination since it is sensitive to the composition of the filled molecular orbitals in a given system^{2c} (regardless of the assignment of formal metal and ligand oxidation states), and therefore not exclusively sensitive to the number of electrons in the system.

Because of the existence of other coordination geometries in pentacoordination, the utility of the correlation diagram for five-coordinate tetragonal systems is somewhat limited. Recently, several 22-electron systems have been found to be trigonal bipyramidal with linearly coordinated nitrosyl groups in either the axial or equatorial positions.^{2k,10,11} These results indicate that it is possible to avoid placing electrons in strongly antibonding orbitals while simultaneously preserving the linear mode of NO coordination *via* a different spatial arrangement of ligands about the metal ion and a consequent reordering of the metal-based d functions. A proposed¹² energy level ordering for trigonal-bipyramidal complexes containing axial nitrosyls has the ligand-field levels ordered as a₁(z²) > e(($\pi^*(\text{NO})$), (xz, yz)) > e(x² - y², xy) > e((xz, yz), ($\pi^*(\text{NO})$)) with the highest filled orbitals in a 22-electron system such as RuH(NO)(P(C₆H₅)₃)₃ being the *weakly* σ^* functions e(x² - y², xy). A detailed correlation of the tetragonal systems with these other geometries is possible, but it requires a knowledge of the energy level orderings for the intermediate transition-state structures between

(7) Because d_{z²} and d_{x²-y²} transform under the same irreducible representation in C_s symmetry, the orbital designations for their two levels are somewhat arbitrary, and both levels should be viewed simply as strongly antibonding σ^* levels based on the metal.

(8) (a) A. Tullberg and N. G. Vannerberg, *Acta Chem. Scand.*, 1180 (1966); (b) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970).

(9) C. S. Pratt, B. A. Coyle, and J. A. Ibers, American Crystallographic Association Abstracts, Summer Meeting, 1971, Ottawa, Canada, Abstract No. C8; C. S. Pratt and J. A. Ibers, quoted in ref 2i.

(10) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

(11) C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3050 (1971).

(12) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, submitted for publication.

the different geometries assuming a specific rearrangement mechanism such as Berry pseudorotation.¹³ The structures of the different five-coordinate 22-electron systems serve to indicate the various energetic minima on the potential surface for five-coordinate nitrosyl complexes, and these results underscore the dual coordinating ability of the nitrosyl ligand which makes these different relative minima possible. Recent studies by Collman, *et al.*,¹⁴ and experimental observations by Wilson and Osborn¹⁵ indicate that the barriers for interconversion between these minima in certain five-coordinate nitrosyl complexes may be relatively low. Collman, *et al.*,¹⁴ have described these interconversions involving the tetragonal-pyramidal form of C_s symmetry and the trigonal-bipyramidal structures as intramolecular redox reactions.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant No. GP-23139) for support of this work. We also wish to thank Professors R. G. Lawler, H. B. Gray, A. Davison, J. A. Osborn, and M. R. Churchill for their helpful comments.

(13) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(14) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, **93**, 1788 (1971).

(15) S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

(16) National Institutes of Health Predoctoral Fellow, 1969–1971.

Cortlandt G. Pierpont,¹⁶ Richard Eisenberg*

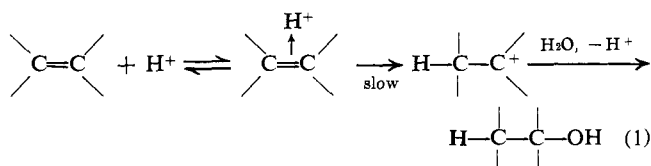
Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received May 3, 1971

General Acid Catalysis in the Hydration of Simple Olefins. The Mechanism of Olefin Hydration

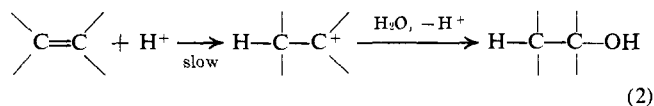
Sir:

The first thorough-going investigation of the mechanism of acid-catalyzed hydration of simple olefins produced the hypothesis that this reaction occurs through rapid and reversible formation of a π -complex intermediate; this intermediate then undergoes rate-determining collapse to a carbonium ion, which is hydrated in a subsequent fast reaction (eq 1).¹ This



reaction mechanism (A-1) was based principally upon three criteria, (1) kinetic acidity dependence in concentrated acids,¹ (2) solvent isotope effects,² and (3) entropies of activation,^{1b,3} each of which was considered to be firmly diagnostic at the time but has since been shown to be incapable of ruling out a mechanism (A-SE2) which circumvents the π -complex intermediate (eq 2).⁴ Recent measurements of volumes of activa-

tion⁵ as well as solvent isotope effects in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures⁶ have in fact been interpreted in terms of an A-SE2 mechanism.



A firm decision between A-1 and A-SE2 mechanisms can be made on the basis of the presence or absence of general acid catalysis, and the detection of this form of catalysis in the hydration of functionally substituted olefins such as styrenes,⁷ vinyl ethers,⁸ enamines,⁹ and ketene acetals¹⁰ has in fact led to the adoption of A-SE2 mechanisms for these reactions. The hydration of simple olefins has also been examined for general acid catalysis, but no reliable conclusion could be reached,¹¹ and the mechanism of this reaction has consequently remained in doubt. We wish to report here that we have now gained evidence which shows that general acid catalysis is present in the hydration of *trans*-cyclooctene and 2,3-dimethyl-2-butene.

It is difficult to examine the hydration of ordinary olefins for general acid catalysis because these substrates are comparatively unreactive. If general catalysis is to be established unequivocally, it should be demonstrated in dilute solution where the interpretation of salt effects is straightforward. This means that the catalysts must be fairly weak acids; otherwise, they will not remain sufficiently undissociated. Carboxylic acids meet this requirement, and buffers of these acids have traditionally been used for this purpose, but even olefins whose hydration generates tertiary carbonium ions react inconveniently slowly in these solutions. Recent investigations of A-SE2 reactions have shown, however, that some general acids, such as H_3PO_4 and HSO_4^- , have anomalously large catalytic coefficients;¹² these acids should therefore be especially suitable for the investigation of slow reactions to which conventional buffer techniques cannot be applied. We have found, in fact, that *trans*-cyclooctene and 2,3-dimethyl-2-butene react at convenient rates in phosphoric acid and bisulfate buffers above 50°.

We measured rates of hydration of these two olefins, by monitoring the decrease in uv absorption at 200 nm, in series of $\text{H}_3\text{PO}_4-\text{H}_2\text{PO}_4^-$ and $\text{HSO}_4^--\text{SO}_4^{2-}$ buffer solutions of constant buffer ratio but changing buffer concentration. In each case, rates of reaction decreased

Solvent isotope effects: V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960); A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1967). Entropies of activation: M. A. Matesich, *J. Org. Chem.*, **32**, 1258 (1967).

(5) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964); **43**, 2453 (1965).

(6) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965).

(7) W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).

(8) P. Salomaa, A. Kankaanpera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); A. J. Kresge and Y. Chiang, *J. Chem. Soc. B*, 53 (1967).

(9) E. J. Stamhuis and W. Maas, *Recl. Trav. Chim. Pays-Bas*, **82**, 1155 (1963); *J. Org. Chem.*, **30**, 2156 (1965); P. Y. Sollenberger and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4261 (1970).

(10) A. Kankaanpera and H. Tuominen, *Suom. Kemistilehti B*, **40**, 271 (1967); V. Gold and D. C. A. Waterman, *Chem. Commun.*, **40** (1967); *J. Chem. Soc. B*, 839, 849 (1968); T. S. Straub, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill., 1970.

(11) (a) F. G. Ciapetta and M. Kilpatrick, *J. Amer. Chem. Soc.*, **70**, 639 (1948); (b) J. L. Jensen, *Tetrahedron Lett.*, 7 (1971).

(12) J. M. Williams and M. M. Kreevoy, *Advan. Phys. Org. Chem.*, **6**, 67 (1968); A. J. Kresge, S. Slae, and D. W. Taylor, *J. Amer. Chem. Soc.*, **92**, 6309 (1970); A. J. Kresge and Y. Chiang, unpublished work.

(1) (a) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5372 (1952); (b) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

(2) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

(3) P. Riesz, R. W. Taft, Jr., and R. H. Boyd, *ibid.*, **79**, 3724 (1957).

(4) Kinetic acidity dependence: F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957); R. W. Taft, N. C. Deno, and P. S. Skell, *Annu. Rev. Phys. Chem.*, **9**, 287 (1958); R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Amer. Chem. Soc.*, **82**, 4729 (1960).