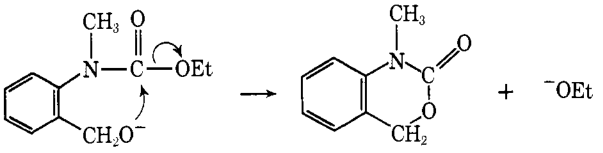
completely ionized species, as in eq 3. This is possibly a consequence of the fact that the carbonyl group of carbamate esters is deactivated by the adjoining nitrogen so that the transition state for formation of a tetrahedral intermediate will be difficult to attain, necessitating attack by a fully developed negative charge. It is possible that decomposition of a tetrahedral intermediate is rate determining with III and IV, but this is unlikely with II because of the excellent leaving group, *p*-nitrophenoxide ion.

A neighboring alkoxide ion is also an efficient intramolecular nucleophile when the leaving group is poor. The similarity in the rates of cyclization of III and IV


IV

indicates that the mechanism is the same for both compounds and must involve intramolecular nucleophilic attack. The pK_a of the hydroxymethyl group is undoubtedly comparable to that of ethanol. The ionized species is therefore sufficiently basic to displace ethoxide. Christenson has determined the rate constants for hydroxide ion catalyzed hydrolysis of ethyl carbanilate and ethyl *N*-methylcarbanilate at 25°. These values are given in Table IV. The k_{OH} value for IV is 1.3×10^6 greater than that for ethyl *N*-methylcarbanilate.

Calculation of the effective molarity of the neighboring hydroxymethyl groups in the present study depends upon an evaluation of k_I from eq 8. This rate constant can only be approximated since K_a cannot be directly measured. There is no significant negative deviation of points in the linear plots of log k_{obsd} *vs.* pH at pH values as high as 13. Therefore, it is likely that pK_a for compounds I–IV is no lower than 14. From the rate constants in Tables II and IV, a minimum value of the effective molarity of the neighboring alkoxide ion of II can then be estimated as 10^5 *M*. Thus, the efficiency of the intramolecular reaction involving an alkoxide ion is only slightly less than that for phenoxide ion (eq 1) even though a kinetically less favorable six-membered ring transition state is being formed. Bruice and Pandit[17] found that a neighboring carboxylate anion is more effective by a factor of 230 when the transition state is five membered rather than six. Taking this into account, the phenoxide and alkoxide intramolecular groups are about equal in catalytic efficiency. Thus, once again an extremely high effective molarity has been found for an oxygen anion nucleophile. Previously, a value of about 10^8 *M* had been estimated for a carboxylate anion nucleophile.[18] These values are much larger than have been found to date for neutral nitrogen nucleophiles, the largest being 5×10^3 *M* for the dimethylamino group of phenyl λ-dimethylaminobutyrates in comparison with trimethylamine attack on substituted phenyl acetates.[19] The neighboring pyridine in substituted phenyl β-pyridylethyl carbonate has effective molarities of from 30 to 50 *M*, depending on the substituent group, in comparison with bimolecular attack of pyridine on ethyl (substituted phenyl) carbonates.[20] A neighboring amide group, where a negatively charged nucleophile participates, increases the rate of hydrolysis of a methyl ester by 10^5.[21] While proper orientation of the nucleophile to the carbonyl group in these compounds is undoubtedly of importance in leading to the highly efficient intramolecular reactions, still it is probable that other factors are also involved. Correct orientation would not explain why anionic nucleophiles are relatively so superior to neutral nitrogen nucleophiles in intramolecular reactions. One possibility is that desolvation of anionic nucleophiles is not as energetically unfavorable in intramolecular reactions as in corresponding bimolecular cases.

That alkoxide ions are extremely powerful intramolecular nucleophiles is of interest in regard to the mechanism of action of α-chymotrypsin since it is the hydroxymethyl group of serine-195 that is acylated during the enzyme reaction with ester and amide substrates.[2] Acylation, proceeding through an enzyme–substrate complex, can be considered quite analogous to an intramolecular reaction. The mechanism generally considered to be most probable involves partial removal of the proton on the serine hydroxyl by histidine-57 acting as a general base. It is clear that the serine oxygen will be a powerful nucleophile in an intracomplex reaction.

Acknowledgment. This work was supported by a research grant from the National Institutes of Health.

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[17] T. C. Bruice and U. K. Pandit, *J. Amer. Chem. Soc.*, **82**, 5858 (1960); see also E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960). They found that the ratio of the rates varies with the para substituent of phenyl esters from 125 with *p*-COOCH$_3$ to 200 for *p*-Cl in hydrolysis reactions assisted by a neighboring carboxylate when compounds forming five- and six-membered ring intermediates are studied.

[18] T. C. Bruice and A. Turner, *ibid.*, **92**, 3422 (1970).

[19] T. C. Bruice and S. J. Benkovic, *ibid.*, **85**, 1 (1963).

[20] J. E. C. Hutchins and T. H. Fife, unpublished data.

[21] R. Shafer and H. Morawetz, *J. Org. Chem.*, **28**, 1899 (1963).

Communications to the Editor

Binary Mixed Dinitrogen Dioxygen Complexes of Nickel. $(N_2)Ni(O_2)$ and $(N_2)_2Ni(O_2)$

Sir:

One of us (G. A. O.) has recently reported matrix isolation infrared and laser Raman spectroscopic evidence for the binary dinitrogen complexes $Ni(N_2)_n$ where $n = 1$–4, formed in the cocondensation reaction of monatomic nickel vapor with pure N_2 and dilute N_2/Ar matrices.[1] The mode of bonding of the di-

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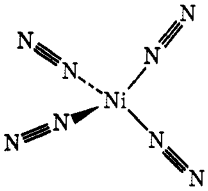
[1] H. Huber, E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Amer. Chem. Soc.*, **95**, 332 (1973).

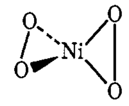
nitrogen ligand to the nickel atom was proven, from $^{14}N^{15}N$ isotopic substitution, to be "end-on." A relationship between these dinitrogen compounds and N_2 chemisorbed onto bulk nickel has also been recently discussed.[2] Using similar matrix cocondensation techniques, binary dioxygen complexes of nickel, $Ni(O_2)$ and $(O_2)Ni(O_2)$, have also recently been characterized[3] and the mode of bonding of the O_2 ligand to the nickel atom was proven from $^{16}O^{18}O$ isotopic substitution to be "side-on." Binary dioxygen compounds of this type may be considered to be model chemical subunits for more complex synthetic and naturally occurring dioxygen carriers.

On comparing $Ni(N_2)_4$ (I), which is isostructural and isoelectronic with the well known complex nickel tetracarbonyl, with $(O_2)Ni(O_2)$, which has been shown to have a unique D_{2d} "spiro" type structure (II) shown below, one might consider each dioxygen in $(O_2)Ni(O_2)$ to be occupying two coordination sites, thus satisfying the valence requirements of tetrahedral Ni(0), as do the four "end-on" bonded dinitrogen molecules in $Ni(N_2)_4$.



T_d

I



D_{2d}

II

It occurred to us that the cocondensation reaction of nickel atoms with dilute $^{16}O_2/^{14}N_2/Ar$ mixtures, might prove to be a simple and direct route to the first examples of transition metal complexes containing *both* molecular dinitrogen and molecular dioxygen coordinated to the same metal atom.

Using experimental techniques similar to those described previously[4] we have investigated the products of the nickel atom $^{16}O_2/^{14}N_2/Ar$ = 1/1/200 cocondensation reaction using matrix isolation infrared spectroscopy and $^{14}N_2/^{15}N_2$, $^{16}O_2/^{18}O_2$ isotopic substitution. The spectrum obtained on the initial deposition at 4.2°K showed all of the lines associated with the known compounds $Ni(N_2)_n$ (where n = 1–4), $(O_2)Ni(O_2)$ and $Ni(O_2)$ which were easily identified and will not be further discussed.[1]

A *single* new line is observed in the N–N stretching region at 2242 cm^{-1} as well as a *single* new line in the O–O stretching region at 977 cm^{-1} (Figure 1A and Table I). Using $^{16}O_2/^{14}N_2/^{15}N_2/Ar$ = 2/1/1/400 mixtures the single line originally at 2242 cm^{-1} becomes a *doublet* at 2242 and 2166 cm^{-1} proving it to correspond to a species containing a single dinitrogen molecule. Similarly, the line originally at 977 cm^{-1} also becomes a *doublet* at 977 and 925 cm^{-1} using $^{16}O_2/^{18}O_2/^{14}N_2/Ar$ = 1/1/2/400 mixtures proving it to correspond to a species containing a single dioxygen molecule. The diffusion characteristics of the absorptions at 2242 and 977 cm^{-1} parallel each other during warm-up experiments and can be assigned to a single chemical species.

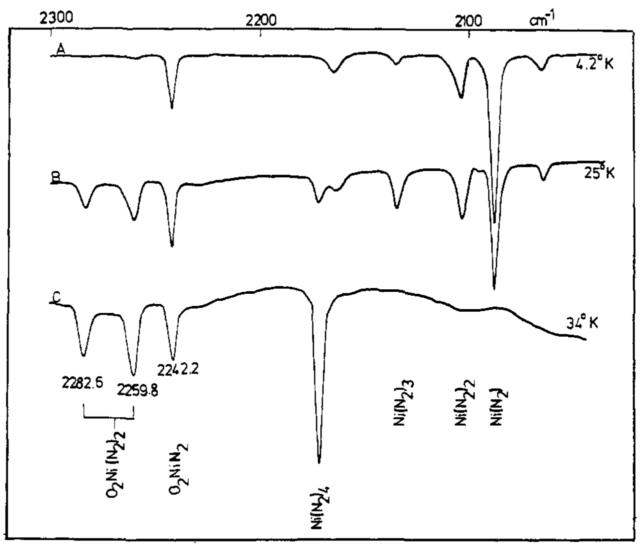


Figure 1. The matrix infrared spectrum in the N–N stretching region, of the products of the cocondensation reaction of Ni atoms with $^{14}N_2$:$^{16}O_2$:Ar = 1:1:200 at (A) 4.2°K and (B, C) after warm-up to 25 and 34°K and recooling to 4.2°K before recording the spectra.

The data described above for dilute $O_2/N_2/Ar$ matrices serve to characterize the new complex as containing a *single* dinitrogen and a *single* dioxygen ligand coordinated to a single nickel atom, that is, monodinitrogen monodioxygen nickel, $(N_2)Ni(O_2)$ (III).

Table I. Vibrational Assignments for the N–N and O–O Stretching Modes of $(N_2)Ni(O_2)$ and $(N_2)_2Ni(O_2)$

Isotopic molecule	$\nu(^{14}N^{14}N)$	$\nu(^{15}N^{15}N)$	$\nu(^{16}O^{16}O)$	$\nu(^{18}O^{18}O)$
$(^{14}N_2)Ni(^{16}O_2)$	2242		977	
$(^{15}N_2)Ni(^{16}O_2)$		2166	977	
$(^{14}N_2)Ni(^{18}O_2)$	2242			925
$(^{14}N_2)_2Ni(^{16}O_2)$	2283			
	2260		972	
$(^{14}N_2)(^{15}N_2)Ni(^{16}O_2)$	2273	2195	972	
$(^{15}N_2)_2Ni(^{16}O_2)$		2207		
		2184	972	
$(^{14}N_2)_2Ni(^{18}O_2)$	2283			
	2260			921

On allowing the original $^{16}O_2/^{14}N_2/Ar$ = 1/1/200 matrix to warm up to 30–35°K, *two new* lines in the N–N stretching region at 2283 and 2260 cm^{-1} grow in rapidly (Figure 1B and 1C) together with a *single new* line in the O–O stretching region at 972 cm^{-1}. These new N–N and O–O absorptions continue to grow in intensity during warm-up experiments at the expense of the lines previously assigned to $(N_2)Ni(O_2)$ and strongly suggest that a second compound is being formed, in a diffusion controlled reaction of $(N_2)Ni(O_2)$ in the matrix. The identity of this new complex was established from the corresponding warm-up data at 30–35°K, using the mixed isotopic matrix gases $^{16}O_2/^{14}N_2/^{15}N_2/Ar$ = 2/1/1/400 and $^{16}O_2/^{18}O_2/^{14}N_2/Ar$ = 1/1/2/400. For example, when $^{16}O_2/^{14}N_2/^{15}N_2/Ar$ mixtures were used (Table I) the N–N stretching modes originally at 2283 and 2260 cm^{-1} in $^{16}O_2/^{14}N_2/Ar$ mixtures became a sextet pattern, showing *three* absorptions in the $^{14}N_2$ region (2283, 2273, and 2260

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(2) M. Moskovits and G. A. Ozin, *J. Chem. Phys.*, 58, 125 (1973).

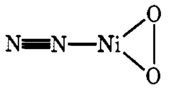
(3) H. Huber and G. A. Ozin, *Can. J. Chem.*, 50, 3746 (1972).

(4) E. P. Kündig, M. Moskovits, and G. A. Ozin, *J. Mol. Struct.*, 14, 137 (1972).

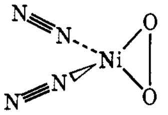
cm^{-1}) and *three* absorptions in the $^{15}N_2$ region (2207, 2195, and 2184 cm^{-1}). These data prove that the species giving rise to the N–N stretching modes at 2283 and 2260 cm^{-1} contains *two* dinitrogen ligands, most probably in a cis configuration.

The O–O stretching mode originally at 972 cm^{-1} in $^{16}O_2/^{14}N_2/Ar$ mixtures produces a *doublet* pattern at 972 and 921 cm^{-1} in $^{16}O_2/^{18}O_2/^{14}N_2/Ar$ mixtures. These data prove that the species giving rise to the O–O stretching mode at 972 cm^{-1} contains a single dioxygen ligand. The diffusion characteristics of the absorptions at 2283, 2260, and 972 cm^{-1} parallel each other during warm-up experiments and can be assigned to a single chemical species containing *two* dinitrogen and *one* dioxygen ligand coordinated to a single nickel atom, that is, bis(dinitrogen)monodioxygennickel, $(N_2)_2Ni(O_2)$ (IV).

The preliminary experiments have shown that binary mixed dinitrogen–dioxygen complexes of nickel are capable of existence under conditions of matrix isolation. From the number and frequencies of the N–N and O–O stretching modes (compared to their parent molecules $Ni(N_2)_n$ and $Ni(O_2)_m$ where $n = 1$–4 and $m = 1$–2), their diffusion behavior and $^{14}N_2/^{14}N^{15}N/^{15}N_2/^{16}O_2/Ar$ and $^{16}O_2/^{16}O^{18}O/^{18}O_2/^{14}N_2/Ar$ isotope multiplet patterns, we conclude that the new complexes are $(N_2)Ni(O_2)$ and $(N_2)_2Ni(O_2)$, containing "side-on" bonded dioxygen and "end-on" bonded dinitrogen in both complexes. Further experiments are presently in progress, and we are also extending these reactions to include Pd and Pt.



III



IV

The discovery and characterization of mixed dinitrogen dioxygen transition metal complexes should prove to be of considerable importance in assessing the bonding characteristics of O_2 and N_2 ligands when coordinated to the same metal atom and when competing with each other for bonding electrons.

Of greater importance, however, is the realization that mixed dinitrogen dioxygen complexes could conceivably have a transient existence in those biological systems, which have the property of fixing dinitrogen or carrying dioxygen in an atmosphere composed of the mixed ligands themselves. In this context we note that purified nitrogenase from Azobacter and Clostridia is rapidly inactivated by O_2; the Mo-Fe protein and the Fe protein are both O_2 sensitive.[5]

Acknowledgments. We wish to thank the Deutscher Akademischer Austauschdienst for a scholarship (W. E. K.) and the National Research Council of Canada and the Research Corporation for financial assistance.

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(5) R. W. F. Hardy, R. C. Burns, and G. W. Parshall in "Bioinorganic Chemistry," R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1971, p 219.

W. E. Klotzbücher, G. A. Ozin*
Lash Miller Chemistry Laboratories and Erindale College
University of Toronto
Toronto, Ontario, Canada

Received January 8, 1973

Stable Carbocations. CXLVIII.[1] 3-Nortricyclyl Cations. The Continuity of the Mode of Charge Delocalization in Carbocations with or without Significant Bridging

Sir:

We have discussed extensively in our preceding work the question of σ-bond delocalization (bridging) in carbocations *via* two-electron, three-center bond formation (carbonium ion formation).[2] A mechanism concerning the ability of strained σ bonds in stabilizing neighboring cationic centers without significant movement of the involved nuclei has recently been suggested ("vertical stabilization") by Traylor.[3] Accordingly strained (or polarizable) σ bonds may stabilize neighboring cationic centers by electronic interaction without concurrent nuclear movement, *i.e.*, *without* altering the length or angles around such bonds as the transition state is approached. Qualitative theoretical treatments of carbenium ion systems which are stabilized through hyperconjugation (σ–p delocalization) are available.[4,5] As interesting as Traylor's suggestion is,[3] according to theoretical considerations the electronic hyperconjugative interaction will *always* be accompanied by some geometrical readjustment (in the Frank–Condon sense, *i.e.*, electronic movement is always accompanied by nuclear movement). The extent of such deformation, however, can vary greatly in different systems. Hoffmann, *et al.*,[6a] recently emphasized that there is *no* dichotomy between participation with or without bridging based on theoretical grounds. Hehre and Hiberty[6b] further cautioned about the importance of vertical stabilization in theoretical studies.

In order to gain more insight into the problem of carbenium ion stabilization by hyperconjugation with or without bridging, we have now chosen a system wherein the strained C–C σ bonds are locked in a rigid framework which prohibits bridging due to the geometrical rigidity, *i.e.*, the 3-nortricyclyl cations.[7]

Among the neighboring groups which are able to stabilize cationic centers whether through hyperconjugation or bridging, the effect of the cyclopropyl group

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(1) Part CXLVII: G. A. Olah, G. Liang, and P. W. Westerman, *J. Amer. Chem. Soc.*, submitted for publication.

(2) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, R. S. Brown, and N. A. Clinton, *ibid.*, **92**, 5228 (1970); (c) T. G. Traylor, H. J. Berwin, and W. Hanstein, *ibid.*, **92**, 829 (1970); (d) T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967).

(4) (a) R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933); **3**, 520 (1935); **7**, 339 (1939); (b) for review, see M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(5) For various discussions on the problem of hyperconjugation, see, for example (a) V. I. Maksimov, *Tetrahedron*, **21**. 687 (1965); (b) T. D. Goldman, *ibid.*, **28**, 3175 (1972); (c) A. Brown and G. H. Schmidt, *Can. J. Chem.*, **50**, 2432 (1972).

(6) (a) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, **94**, 6221 (1972); (b) W. J. Hehre and P. C. Hiberty, *ibid.*, **94**, 5917 (1972).

(7) (a) C. C. Lee and B. S. Hahn, *J. Amer. Chem. Soc.*, **92**, 2583 (1970); (b) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; (c) M. Simonett and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954); (d) J. Paasivirta, *Justus Liebigs Ann. Chem.*, **686**, 1 (1965); (e) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972); (f) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (g) S. Winstein, *Quart. Rev., Chem. Soc.*, 141 (1969); (h) P. R. Story and B. C Clark, Jr., "Carbonium Ions," Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., in press, Chapter 23.