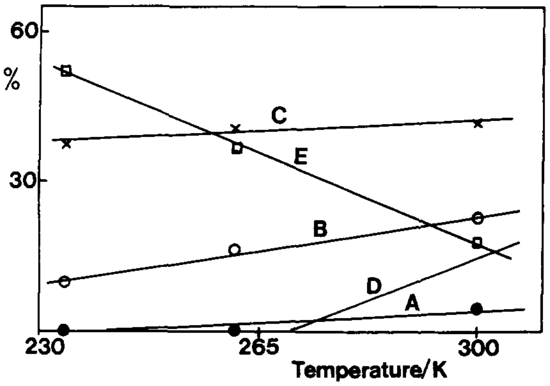

Figure 3. The variation with temperature of resolved component areas (expressed as percent of the total band area) for liquid ammonia solutions of NaCN at $r = 19.3$.

perature and/or concentration. The frequencies of Y and E are identical. The frequency of X is the same as that of D, but this may be coincidental as D is not firmly characterized by the spectra.

Solutions of alkali metal salts of nitrates, nitrites, thiocyanates, azides, and perchlorates also give unexpectedly complex Raman bands which change form with changes of concentration, temperature, and counterion. Bands of these anions have been resolved into components as follows. (Na^+ and Li^+) NO_3^-: ν_1, 2 components; ν_3, 3; ν_4, 2. $K^+NO_3^-$: ν_1, 1; ν_3, 2; ν_4, 1. $Na^+NO_2^-$: ν_1, 3; ν_2, 4. $K^+NO_2^-$: ν_1, 2; ν_2, 2. $Na^+N_3^-$: ν_1, 3; $2\nu_2$, 3. $K^+N_3^-$: ν_1, 3; $2\nu_2$, 2. (Na^+ and Li^+)SCN^-: ν_1, 3; ν_3, 3. (K^+ and Cs^+)SCN^-: ν_1, 2; ν_3, 2. (Na^+ and K^+)ClO_4^-: ν_1, 1; ν_2, 1; ν_4, 1.[6]

It is possible to present a satisfactory individual anion-specific explanation for many multicomponent bands. Thus, linkage isomerism of contact ion-pair species is possible for NO_2^-,[8] NCS^-,[8] and CN^-.[9] Alternatively, solvent-anion interaction through hydrogen bonding is possible, and has indeed been proposed for the NCS^- ion in liquid ammonia.[10] A similar mechanism has been suggested to account for the ν_3 region of the NO_3^- spectrum, where hydrogen bonding lifts the degeneracy of the asymmetric N-O stretching vibration.[10] In ammonia the corresponding band is much less broad than in water, though we consider the band to be more complex than has been suggested.[10-12]

Contrary to these specific explanations are the trends, common to all anions studied, that: (i) the component at lowest frequency increases in relative intensity as concentration and temperature are decreased; (ii) solutions with K^+ as counterion mostly give less complex spectra than solutions with Na^+ as counterion. While not excluding the possibility that some anion-specific effects are operative, we propose an explanation which is common to all anions studied. That is, that the resolved components of a complex band are directly attributable to discrete forms of contact, solvent-shared, solvent-separated ion-pairs and unpaired, solvated, "free" anions.

In a solution as concentrated as those considered in these studies, and particularly where $r < 20$, a high degree of short-range ordering of ions and solvent molecules into quasi-lattice structures must be expected. Within such a framework it is highly probable that an anion may be found in a variety of locally structured groups.[1] The proportion of such ion-aggregates would be expected to be concentration, cation, and temperature dependent.

Assignment of band-components to individual ion-paired species is not possible at the present time, since we cannot measure spectra from solutions sufficiently dilute to permit unambiguous assignment for the "free" anion. The lowest concentration that we have been able to study satisfactorily is $r = 1017$ (KCN solution) which is still far above the acceptable upper concentration limit for electrochemical studies of ion-pairing. It is also clear from such studies on liquid ammonia systems[13] that even at a concentration of $r \simeq 10^6$ the solute is still substantially in an ion-paired form. Thus we can confidently assign the lowest frequency component within each band only to the least associated anionic species. Nevertheless, the correlation of bands E, C, B, and A in the NaCN solution spectra with the "free" ion, solvent-separated, solvent-shared, and contact ion-paired species would be consistent with the presently available evidence.

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(5) Spectra were recorded at spectral slit-width of 0.5 cm^{-1}. Frequencies are accurate to ±2 cm^{-1}. Bands were resolved into components using the Gauss–Lorenz shape-function $I_\nu = h\{(1 - f)/[1 + (2(\nu - \nu_0)/w)^2] + f \exp[-\log_e 2 \times (2(\nu - \nu_0)/w)^2]\}$, where h is the height, w the width at half-height, ν_0 the position, and f the fraction of Gaussian contribution to each component. f was the same for all components and was optimized for each band. In some NaCN spectra a significant improvement in fit was achieved upon introducing the band D at ca. 2062 cm^{-1}. The intensity of this band decreased sharply with temperature. Although the computed intensity of D showed consistent trends in frequency and intensity, we cannot be certain that it is not a computational artefact.

(6) Both the ν_2 and ν_4 bands of ClO_4^- decreased in half-width with decreasing temperature, with a concomitant change in shape-function. A symmetric band was found as observed previously.[7]

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The Role of Water in the Rhodium(I) Catalyzed Reduction of Nitric Oxide by Carbon Monoxide. An Isotope Labeling Study

Sir:

It has previously been reported that the complex $[RhCl_2(CO)_2]^-$ in aqueous acidic ethanol catalyzes the carbon monoxide reduction of nitric oxide according to eq 1 under mild conditions.[1,2]

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (1)$$

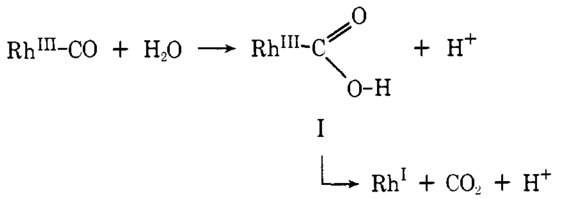
In this environmentally important reaction, water was found to be cocatalytic and intimately related to product formation.[2] Based on the CO reduction of Rh(III) to Rh(I)[3] and the known decomposition of hyponitrous acid,[4] we proposed that water is both consumed in the production of CO_2 and regenerated in the formation of N_2O. We now report an isotope labeling study which proves this contention by showing that the oxygen in the product CO_2 is derived from water in the reaction medium, and not directly from the nitric oxide reactant. Thus water serves as the means by which oxygen is transferred in this stoichiometrically simple, but mechanistically complex reaction. Our study also reveals that intermediate I in reaction 2 exhibits virtually no tendency for back reaction and exchange

Table I. Observed and Calculated Isotopic Abundance of the CO_2 Product

	Run 1		Run 2	
	Isotopic abundance[a]		Isotopic abundance[b]	
Mass	Obsd	Calcd[c]	Obsd	Calcd
44	0.76	0.76	0.83	0.81
46	0.234	0.244	0.166	0.190
48	0.0087	0.000 49	0.0064	0.000 38

[a] NO:CO = 1:2, N for H_2O = 0.243; N for CO_2 product: 0.126 obsd, 0.123 calcd. [b] NO:CO = 2:1, N for H_2O = 0.189; N for CO_2 product: 0.0894 obsd, 0.0954 calcd. [c] Assuming 50% of the oxygen is derived from H_2O.

of the carbonyl oxygen relative to decarboxylation and product formation.



(2)

The experiments described herein use ^{18}O labeled water and a flow reactor designed to sweep product gases from solution in a manner similar to that employed by Posey and Taube[5] in their study of the aquation of cobalt carbonato complexes. In this way isotopic equilibration of the product CO_2 with labeled water in the reaction medium is prevented. In each of the experiments the appropriate flow of mixed NO and CO was passed through a supporting glass frit and the reaction solution. The gas flow then proceeded through a series of dry ice traps, and the CO_2 and N_2O products were finally condensed in a trap cooled with pentane slush. Chromatographic separation of the product gases using a Porapak Q column resulted in the collection of pure CO_2 which was then analyzed on a mass spectrometer (at m/e 44, 46, and 48) with no interference from N_2O (44) or traces of ethanol (46). The mass spectrometer was an Atlas MAT CH-4, and the isotopic distribution of $C^{16}O_2$, $C^{18}O^{16}O$, and $C^{18}O_2$ was determined from the average peak heights of triplicate spectra. Reaction solutions were analyzed for exchangeable oxygen after the runs by equilibration with a small amount of CO_2, which was then separated and analyzed on the mass spectrometer.

Two control experiments established that our flow reactor did indeed remove the product CO_2 from the reaction solution much faster than the CO_2 could reach isotopic equilibrium with the labeled water present. First, CO_2 was bubbled slowly (~2 cm^3/min) through the reaction solution in a stream of dry carbon monoxide and nitrogen (~25 cm^3/min). The solution contained 0.010 M $(Ph_4As)[RhCl_2(CO)_2]$ in 25 ml of absolute ethanol to which 0.20 ml of isotopically labeled water and 3.2 mmol of dry HCl gas (equivalent to 0.27 ml of concentrated HCl) had been added. The mole fraction of ^{18}O (denoted hereafter by N) at natural abundance was verified as 0.0020 with the CO_2 cylinder at hand. The isotopic composition of the CO_2 which had been bubbled through the reaction solution was unchanged within experimental error (±5%), while N for the water in the solution equaled 0.107. Since much of the CO_2 bubbled through this solution may never have dissolved, a second control experiment was designed to have the CO_2 gas originate as molecular CO_2 in solution. Here, the same amount of water and ethanol was placed in the reactor, and a small amount of $NaHCO_3$ was added while bubbling through dry nitrogen at ~40 cm^3/min. A slow flow of dry HCl was then added to the gas stream, generating CO_2 which was trapped, separated, and analyzed to have N = 0.0040. For the water in this solution, N was equal to 0.155 and thus exchange was limited to only 1.3%. This control was chosen since Mills and Urey[6] had previously shown that under these conditions oxygen exchange in HCO_3^- occurs only through the formation of CO_2, eq 3, which in our flow reactor is swept from the solution.

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons H_2O + CO_2 \qquad (3)$$

Two experiments, using different proportions of reactant gases, were done to establish the isotopic composition of the CO_2 product produced by the catalytic reduction of NO in solutions containing labeled water. Each reaction solution contained 25 ml of anhydrous ethanol, 0.40 ml of water with 6.4 mmol of dry HCl gas (equivalent to 0.54 ml of concentrated HCl), and 0.010 M $(Ph_4As)[RhCl_2(CO)_2]$. In the first run the CO flow rate was established first and NO added to the flow until the ratio of NO:CO was 1:2, with a total flow rate of ~40 cm^3/min. In the second run the NO flow rate was established first, converting the starting rhodium complex to the incompletely characterized red species indicated here as $[RhCl_2(NO)_2]^-$ by reaction 4.[2] The gaseous products of this reaction were not collected. Carbon monoxide was then added to the gas flow until the NO:CO ratio was 2:1 with a total flow rate again of ~40 cm^3/min. The results of both of these runs are presented in Table I. The N_2O product was examined and found to be isotopically the same as natural abundance.

$$[RhCl_2(CO)_2]^- + 6NO \rightarrow [RhCl_2(NO)_2]^- + 2CO_2 + 2N_2O \qquad (4)$$

The presence of substantial amounts of labeled oxygen in the CO_2 product given in Table I unequivocally establishes that water is the source of oxygen in the catalysis of (1) by $[RhCl_2(CO)_2]^-$ in aqueous acidic ethanol. The CO_2 product is formed in this reaction via nucleophilic attack on a Rh(III)-coordinated carbonyl as shown in (2), followed by decarboxylation. This path is clearly the most reasonable one consistent with the experimental data. The possibility of a different mechanism for incorporating the water oxygen into the CO_2 product via a rapid exchange between water and coordinated nitrosyl followed by an intramolecular oxygen transfer to CO can be ruled out because substantial amounts of $N_2{}^{18}O$ product, which would be predicted, are not observed. Similarly, other proposals for the specific role of H_2O in the formation of CO_2 are either inconsistent with the results of Table I or are chemically unreasonable. Because of its cocatalytic nature, water must be regenerated in the catalytic cycle, presumably by an acid induced coupling of coordinated nitrosyls to form coordinated hyponitrous acid which then decomposes to N_2O and H_2O.[4] Thus the water molecule serves as the oxygen transfer agent in this catalysis of reaction 1.

The relative stability of the hydroxycarbonyl intermediate I can also be gleaned from the present results. If proton transfer between the two oxygens in I is facile and if I is in chemical equilibrium with the starting Rh^{III}-CO complex, then partial or complete isotopic equilibration of the carbonyl oxygen would be observed in the CO_2 product. Such equilibration has been observed previously by Muetterties for $Re(CO)_6^+$[7] and a similar equilibrium has been reported by Clark and Jacobs[8] for the system $[PtCl(CO)(PEt_3)_2]^+ + H_2O$ which eventually leads to the stable Pt(II) hydride complex. Deeming and Shaw have also isolated a stable Ir(III) hydroxycarbonyl species, $[IrCl_2(COOH)(CO)(PMe_2Ph)_2]$.[9]

However, the present results clearly contrast with the notion of a stable intermediate of structure I, and indicate that decarboxylation to CO_2 product proceeds much more rapidly than back reaction and carbonyl exchange. This fact no doubt contributes to the efficiency of the present catalytic cycle. The best agreement between observed and calculated abundances of the CO_2 product in Table I is obtained when the calculated model assumes a carbonyl oxygen having natural abundance ^{18}O. The slightly higher observed values of doubly labeled CO_2 indicate that exchange of the $C^{16}O^{18}O$ product with labeled water may occur to a maximum extent of 3% which is consistent with the control experiment using HCO_3^- described above.

Thus the present study affirms the oxygen transfer role of water in the $[RhCl_2(CO)_2]^-$ catalyzed reduction of NO by CO and shows that the intermediate hydroxycarbonyl species is unstable to exchange and back reaction relative to CO_2 formation.

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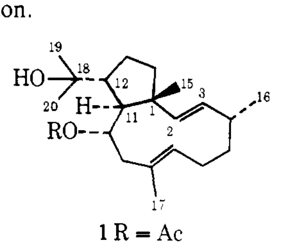
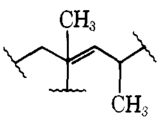
A Novel Diterpene from *Dollabella californica*

Sir:

The sea hare *Dollabella californica* Sterns,[1] a large soft-bodied opistobranch mollusk, was collected at Isla Partida, Gulf of California. The digestive gland of *Dollabella*, like that of *Aplysia californica*,[2] contained a number of terpenoid compounds which are probably of dietary origin. The major components of the digestive gland extracts are a series of diterpenes which appear to be closely related. We wish to report the structural determination by single-crystal x-ray diffraction analysis of a diterpene **1** having a novel 5,11-bicyclic carbon skeleton.



1 R = Ac
2 R = H



3

Florisil chromatography of the acetone extracts of homogenized digestive glands of *Dollabella* resulted in the isolation of six diterpenes, one of which crystallized from hexane, mp 78°, $[\alpha]^{22}\text{D}$ $-101°$ (*c* 1.3). The crystalline material **1** (3% of extract) was shown to have the molecular formula $C_{22}H_{36}O_3$, which, together with bands at 3650 and 1740 cm^{-1} (CCl_4) in the infrared spectrum, suggested that the compound was a monoacetate of a diterpene diol. We were unable to measure the exact mass of the parent ion because of rapid loss of $C_2H_4O_2$; P − 60 gave *m/e* 288.244 while *m/e* 288.245 for $C_{20}H_{32}O$. This was also confirmed by treatment of the acetate **1** with lithium aluminum hydride in anhydrous ether to obtain the corresponding diol **2**, mp 152–153°. The NMR spectrum of **1** contained six methyl signals: a singlet at δ 2.05 due to the acetate, a singlet at 1.62 due to a vinyl methyl, two singlets at 1.25 and 1.18 due to methyl groups on carbon-bearing oxygen, a doublet at 0.94, and a singlet at 0.82 ppm. The low-field region of the NMR spectrum contained an apparent doublet of triplets at δ 4.81 (J = 9, 1, 1 Hz) due to the α-acetoxy proton, a broad triplet at 5.10 (J = 7 Hz) due to the proton on the trisubstituted olefinic bond, and two signals at 5.07 (d, J = 16 Hz) and 5.22 ppm (dd, J = 16, 9 Hz) due to a trans olefin. Irradiation at δ 2.32 caused the double doublet at 5.22 to collapse to a doublet and the doublet at 0.94 to become a sharp singlet, suggesting the partial structure **3**. The ^{13}C NMR spectrum confirmed the presence of two olefinic bonds (δ 135.1, 130.9, 127.8, and 126.84 ppm) and an acetate carboxyl (168.5 ppm) but indicated only two other fully substituted carbon atoms: one at 72.7 ppm bearing hydroxy and two methyl groups, the other at 20.8 ppm bearing a methyl group at a ring junction. The acetate **1** was therefore bicyclic and contained a trans disubstituted olefin, either in a non-isoprenoid sidechain or in a medium-sized ring. Since these constraints could not be accommodated by any known diterpene skeleton,[3] the acetate **1** was subjected to single-crystal x-ray diffraction analysis.

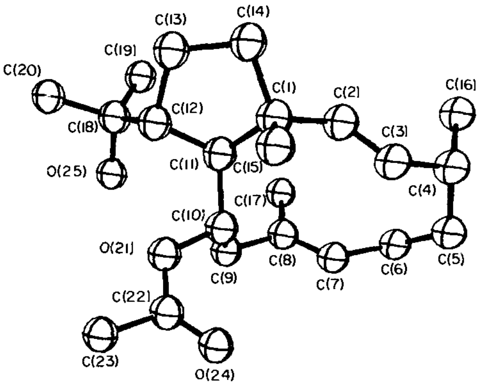


Figure 1. A computer generated perspective drawing of **1**. Hydrogens are not shown, and no absolute stereochemistry is implied.

Crystals of **1** belonged to the common, chiral space group $P2_12_12_1$ with a = 8.778 (1), b = 9.470 (1), and c = 25.785 (2) Å. The density indicated one molecule of $C_{22}H_{36}O_3$ per asymmetric unit. All unique data with $2\theta \leq 114°$ were recorded on a computer controlled four-circle diffractometer using graphite monochromated Cu Kα radiation (1.5418 Å). Periodically monitored check reflections showed no significant crystal deterioration. A total of 1703 reflections were measured and 1540 (90.4%) were judged observed after correction for Lorentz, polarization, and background effects ($F_o^2 \geq 3\sigma(F_o^2)$).

The structure was solved using a multiple solution weighted tangent formula approach.[4] The largest 150 normalized structure factors were phased and a three-dimensional E-synthesis of the best set revealed 19 of the 25 nonhydrogen atoms. Subsequent elaboration of the structure and refinement was uneventful.[5] Full matrix least squares refinements with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogens converged to a final crystallographic residual of 0.033 for the observed reflections. Tables of fractional coordinates, bond distances, bond angles, and observed and calculated structure factors can be found in the supplemental material.

Figure 1 shows a computer generated perspective drawing of **1**. As anticipated from the spectral data the double bond at C(2) is trans. The double bond at C(7) also has the E configuration. The 5- and 11-membered rings are joined in a trans fashion. The work described here does not define the absolute