the vibrational wave functions of a molecule such as NH_3 which inverts between two equivalent pyramidal configurations (Figure 1).[7] If the planar configuration were the most stable, the electronic potential would have the parabolic form shown on the left with simple harmonic vibrational energy levels equally spaced. If a potential hill is raised gradually in the center, the two pyramidal configurations become the most stable and the energy levels approach each other in pairs. For an infinitely high potential hill, the pairs of energy levels are exactly degenerate, as shown on the right. The rise of the central potential hill modifies the wave functions as shown, but does not destroy their parity. The even and odd parity wave functions ψ^+ and ψ^- describe ideal stationary states in all circumstances. It can be seen that the wavefunctions $\psi_0{}^L$ and $\psi_0{}^R$, corresponding to the system in its lowest state of oscillation and localized completely in the left and right wells, respectively, are obtained from symmetric and antisymmetric combinations of the even and odd parity wave functions:

$$\psi_0{}^L = \frac{1}{\sqrt{2}}(\psi_0{}^+ + \psi_0{}^-)$$

$$\psi_0{}^R = \frac{1}{\sqrt{2}}(\psi_0{}^+ - \psi_0{}^-)$$

In fact $\psi_0{}^L$ and $\psi_0{}^R$ are simply the time-independent part of the general wave function[7]

$$\psi_0 = \frac{1}{\sqrt{2}}(\psi_0{}^+ + \psi_0{}^- e^{i\omega t})e^{iW_0{}^+t/\hbar}$$

taken at $t = 0$ and $t = \pi/\omega$, where $\hbar\omega = W_0{}^- - W_0{}^+$ is the energy separation of the two parity states (the tunneling splitting). Thus, if the system is prepared at $t = 0$ in the left well, after a time $t = \pi/\omega$ it will be found in the right well, ω being the frequency of a complete inversion cycle. The tunneling splitting is determined by the height of the potential barrier, and is zero if the barrier is infinite.

Since $\psi_0{}^L$ and $\psi_0{}^R$ are states of mixed parity, the origin of the mixed parity states of a resolved enantiomer is now obvious, for a potential energy diagram with a very high barrier separating the left and right wells can be drawn for any resolvable chiral molecule.[8] If such a state is prepared, but the tunneling splitting is finite, its energy will be indefinite because it is a superposition of two parity states of different energy. Using $\Delta W = \hbar/T$, where T is the average lifetime and ΔW is the width of the level corresponding to a quasi-stationary state,[9] the splitting of the two definite parity states is seen to be proportional to the inverse of the L to R conversion time (cf. the previous paragraph). A crucial point is therefore the relation between the time scale of the optical activity measurement and the lifetime of the resolved enantiomer. A manifestation of the uncertainty principle appears to arise here which may be stated loosely as follows. "If, for the duration of the measurement, there is complete certainty about the enantiomer, there is complete uncertainty about the parity of its quantum state. If there is complete uncertainty about the enantiomer, there is complete certainty about the parity of its quantum state." Thus experimental resolution of the definite parity states in an enantiomer of tartaric acid, say, which has a lifetime probably greater than the age of the universe, is impossible unless the duration of the experiment is virtually infinite, whereas for a nonresolvable chiral molecule such as H_2O_2, spectroscopic transitions between states of definite parity are observed routinely.

Nonresolvable chiral molecules can be regarded as "self-racemic" since the *single* molecules exist in states of definite parity. On the other hand, definite parity states of resolvable chiral molecules must embrace *two* opposite enantiomers, which accords with the usual concept of a racemic mixture. The states of the neutral K meson have been likened to the four possible states of a chiral molecule, the particle and antiparticle states corresponding to $\psi_0{}^L$ and $\psi_0{}^R$, with "racemic" states corresponding to $\psi_0{}^+$ and $\psi_0{}^-$.[10] However, since *single* neutral K mesons can exist in definite parity (more precisely, CP) states with different energies, the analogy would appear to be with a self-racemic chiral molecule such as H_2O_2. The analogue of a resolved enantiomer would appear to be a left or right circularly polarized photon because such a photon is in a state of mixed parity and only the combined states of *two* such photons can have definite parity[3] (this analogy is not exact because the parity operations are carried out in the combined momentum-polarization space of the photon). The use of mixed parity states appears to be essential in any discussion of the symmetry aspects of reactions involving chiral molecules, and interesting parallels with certain elementary particle reactions can be expected.

Although the existence of mixed parity quantum states is a necessary condition for both a permanent electric dipole moment and optical activity, it is not sufficient since a molecule can possess a permanent electric dipole moment without being optically active, and point group symmetry arguments must be introduced to distinguish the two situations. The essential distinction is that, while both the electric dipole moment and the optical rotatory parameter have odd parity, the first is a polar vector while the second is a pseudoscalar. This is why an isotropic collection of molecules can show no bulk electric dipole moment, but can show optical rotation.

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Oxygen Transfer from Ligands: Cobalt Nitro Complexes as Oxygenation Catalysts

Sir:

Recently, catalytic oxidations of phosphines to phosphine oxides[1] and isonitriles to isocyanates[2] and co-oxidation of Ph_3P and terminal olefins to Ph_3PO and 2-alkanones[3] have been demonstrated using metal peroxo complexes. In these oxidations, the formation of strong P=O and RNC=O bonds is an important driving force. Since all known peroxo complexes contain oxidizable ligands, co-oxidation of the ligands cannot be avoided.[17] In addition, coordinatively unsaturated metal complexes which can be easily oxidized or reduced tend to initiate nonspecific Haber-Weiss radical autooxidations.[4]

To avoid these problems, we would like to offer a new approach which involves oxidation of organic substrates via an oxygen atom transfer from a *ligand* of the metal complex. The

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Table I. Catalytic Oxidation of Triphenylphosphine[a]

expt	complex	[Co][b]	Ph_3P/Co	solvent	Ph_3PO/Co[c]
1	Co(saloph)·py·NO_2	6.74	10.0	DCE + 5% py	8.7
2	Co(saloph)·py·NO_2	8.18	4.4	DCE	2.2
3	Co(saloph)·py·NO_2	4.38	5.2	DCE + 5% py + 2.3×10^{-2} M BTBPC	4.8
4	Co(saloph) I	5.08	16.2	DCE + 5% py	0.0
5	Co(saloph)	4.80	6.1	DCE + 5% py	0.5
6	Co(saloph)·Ph_3P·NO_2[d]	5.90	6.0	DCE	0.8

[a] Reaction run for 16 h at 60 °C under 1 atm of O_2 (flow of O_2 = 5-10 mL/min). [b] Cobalt concentration in 10^{-3} M. [c] See ref 10; Ph_3PO/Co values are corrected for autoxidation observed in a control experiment where no metal complex is present. [d] At the end of 16-h period; Co(saloph)·Ph_3P·NO_2 can be recovered unchanged from the reaction solution.

resulting reduced ligand would then be reoxidized by molecular oxygen completing the catalytic cycle. In this system the formal oxidation state of the metal would not change and coordinatively saturated complexes would be preferred.

A logical starting point in this work is the observation by Clarkson and Basolo[5] that five-coordinate cobalt nitrosyl complexes possessing bent geometries react with O_2 at room temperature in the presence of a base to form six-coordinate nitro complexes[6] (eq 1). In these formally Co(III) complexes the NO_2 group is monodentate and N bound. Since the electronic structure of these nitrosyl complexes has been described[5,7] as Co(III)-NO^-, formally reaction 1 takes place without change in the oxidation state of cobalt.

$$\text{LCo-NO} + \text{B} + \tfrac{1}{2}\text{O}_2 \rightarrow \text{B·LCo-NO}_2 \qquad (1)$$

$$\text{L} = \text{tetradentate ligand; B} = \text{base}$$

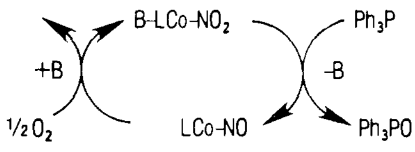
We report that Co(saloph)·py·NO_2 (**1**) (saloph = *N,N'*-bisalicylidene-*o*-phenylenediamino)[8] can be used in the stoichiometric and catalytic oxidation of Ph_3P to Ph_3PO by an oxygen-transfer mechanism.

Oxidation of Ph_3P by **1** was studied in deoxygenated 1,2-dichloroethane (DCE) at 60 °C. Samples were withdrawn at appropriate intervals. After solvent evaporation, the concentrations of the reaction components were monitored by IR observing the loss of **1** (ν_{NO_2} 1320, 1220, and 820 cm^{-1}) and the formation of CoL·NO (ν_{NO} 1660 cm^{-1}) and Ph_3PO (a characteristic band at 720 cm^{-1}).[10] In a reaction containing initially Ph_3P/**1** of 8, **1** reacted completely after 3 h producing Co(saloph)·NO and a stoichiometric amount of Ph_3PO. Under similar conditions, Co(saloph)·NO does not react with Ph_3P. These experiments demonstrate that **1** can oxidize Ph_3P by an oxygen transfer from the nitro ligand as shown by eq 2. The planarity of the saloph ligand and the six-coordinate nature of **1** suggests that the oxidation takes place without prior coordination of Ph_3P to Co in **1**.

$$\text{Co(saloph)·py·NO}_2 + \text{Ph}_3\text{P} \rightarrow \text{Co(saloph)·NO} + \text{Ph}_3\text{PO} + \text{py} \qquad (2)$$

Catalytic oxidation of Ph_3P can be effected when O_2 is present in a solution containing **1**, Ph_3P, and excess pyridine (Table I).[11] The catalytic oxidation can be represented by reactions 1 and 2 (Scheme I). Several facts support this scheme. (1) Stoichiometric experiments demonstrate that **1** oxidizes Ph_3P and that NO does not dissociate during the reaction. (2) During the catalytic oxidation the IR spectrum of the complex (expt 1) remains similar to that of **1** initially added. This demonstrates that NO_2 dissociation is not responsible for the observed oxidation. (3) A radical oxidation can be ruled out since addition of 2,6-bis(*tert*-butyl)-*p*-cresol (BTBPC) does not inhibit Ph_3P oxidation (expt 3). (4) Since neither Co(II)(saloph) nor Co(III)(saloph)I[12] promotes appreciable oxidation, "oxygen activation" routes other than that discussed above may be discounted. (5) Without an excess of pyridine (expt 2) the rate of Ph_3P oxidation decreases. This is consistent with the finding that, under the conditions of expt 2, the majority of complex **1** is converted[13] to Co(saloph)·Ph_3P·NO_2, which is far less effective than **1** as a catalyst for the oxidation of Ph_3P (expt 6).

Scheme I



Dioxo complexes of Mo(VI) such as $O_2Mo(S_2CNR_2)_2$ can oxidize Ph_3P to produce $OMo(S_2CNR_2)_2$ and Ph_3PO.[14] As a gage of the strength of the oxidizing ability of **1**, we investigated its reaction with an excess of $OMo(S_2CNR)_2$ (R = Me, *n*-Pr) and found that after 2 h quantitative oxygen transfer to produce Co(saloph)·NO and $Mo_2O_3(S_2CNR_2)_2$ takes place (eq 3 and 4) under argon in DCE at 60 °C. On the other hand, reaction of $O_2Mo(S_2CNR_2)_2$ with Co(saloph)·NO in DCE-pyridine solvent does not produce a measurable quantity of **1**. These experiments demonstrate that **1** is a stronger oxidant than $O_2Mo(S_2CNR_2)_2$.

$$\text{Co(saloph)·py·NO}_2 + \text{OMo(S}_2\text{CNR}_2)_2 \xrightarrow{-\text{py}} \text{Co(saloph)·NO} + \text{O}_2\text{Mo(S}_2\text{CNR}_2)_2 \qquad (3)$$

$$\text{OMo(S}_2\text{CNR}_2)_2 + \text{O}_2\text{Mo(S}_2\text{CNR}_2)_2 \rightarrow \text{O}_3\text{Mo}_2\text{(S}_2\text{CNR}_2)_4 \qquad (4)$$

In conclusion, this work has demonstrated the feasibility of transferring an oxygen atom from the nitro group of Co(saloph)·py·NO_2 to external Ph_3P[15] and $OMo(S_2CNR_2)_2$. This oxygen transfer is the first example in which the metal formally remains at a constant oxidation state with the redox chemistry occurring only at the ligand. We are currently investigating other nitrosyl/nitro systems with the expectation of finding new, potent oxidizing agents.

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(8) The nitrosyl complex Co(saloph)·NO was prepared by a method analogous to that for Co(salen)·NO:[9] ν_{NO} 1660 cm^{-1}. Anal. Calcd for $CoC_{20}H_{14}N_3O_3$: Co, 14.61; C, 59.56; H, 3.50; N, 10.42. Found: Co, 14.82; C, 59.20; H, 3.66; N, 10.30. The nitrosyl complex was then oxidized by air to the nitro complex **1:** ν_{NO_2} 1320, 1220, and 820 cm^{-1}. Anal. Calcd for $CoC_{25}H_{19}N_4O_4$: Co, 11.82; C, 60.25; H, 3.84; N, 11.24. Found: Co, 12.06; C, 59.86; H, 4.05; N, 11.38.
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quoted are accurate to ±10–15%.

(11) After reaction times of more than 6 h, **1** is gradually decomposed with an accompanying loss of activity for Ph_3P oxidation. After 48 h, when **1** is completely decomposed, oxidation of Ph_3P in the presence of O_2 is not observed.

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(15) This sytem may be compared with the recently reported oxidation of PPh_3 to $OPPh_3$ by a Ru–NO_2 complex.[16] The oxidant $[Ru^{III}(bpy)_2NO_2Cl]^+$ is generated electrochemically from $[Ru^{II}(bpy)_2(NO)Cl]^{2+}$ in the presence of water and a base. In this system, oxidizing equivalents are provided electrochemically instead of by O_2, and 1 mol of hydroxide is needed for every mole of $OPPh_3$ produced.

(16) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.* **99**, 4821 (1977).

(17) NOTE ADDED IN PROOF. Recently H. Mimoun and co-workers (*J. Am. Chem. Soc.*, **100**, 5437 (1978)) described the specific oxidation of terminal olefins to 2-alkanones employing Rh-based catalysts in which terminal olefins are the only oxidizable ligands.

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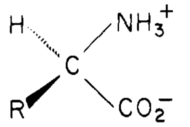
Experimental Determination of the Acidity and Basicity of Glycine in the Gas Phase

Sir:

For many years it has been known that the most stable structure of α-amino acids in aqueous solution and in the crystalline state is best written as a dipolar ion, or zwitterion.



Typically these compounds are appreciably soluble only in water, and as solids they do not melt until they decompose at almost 300 °C.[1] These physical properties are consistent with the "salt-like" dipolar ion structure. There are two ionizable groups in aqueous solution having pK_a values of 2 and 9. Taking glycine as an example, the first pK_a at 2.3 is what one expects for ionization of a carbonyl group (reaction 1). This

$$H_3\overset{+}{N}CH_2COOH = H^+ + H_3\overset{+}{N}CH_2COO^-, \quad \Delta G^\circ = 3.1 \text{ kcal/mol} \quad (1)$$

pK_a value is consistent with that of acetic acid ($pK_a = 4.8$) and the presence of a strong electron-withdrawing effect of the positive ammonium group which stabilizes the glycine dipolar ion.[1] The second acid dissociation for glycine has a pK_a of 9.6 and corresponds to reaction 2. This is similar to ethaneammonium ion having a pK_a of 10.7. Thus, in aqueous solution the basicity of glycine (reaction 1) is similar to that of acetate ion, and the acidity of glycine (reaction 2) is similar to that of an alkylammonium ion.

$$H_3\overset{+}{N}CH_2COO^- = H^+ + H_2NCH_2COO^-, \quad \Delta G^\circ = 13 \text{ kcal/mol} \quad (2)$$

Very little is known about the properties of α-amino acids in the gas phase owing to their extremely low volatility and tendency to decompose at elevated temperatures. Electron impact mass spectrometry on glycine produces a base peak at *m/e* 30, $H_2NCH_2^+$, corresponding to loss of COOH from the neutral molecule.[2] Chemical ionization mass spectrometry using methane,[3] isobutane,[4] and hydrogen[5] as reagent gases has been performed to elaborate the fragmentation mechanisms. However, there are no data in the literature which allow the acidity and basicity of the α-amino acids in the gas phase to be compared with the energetics of their ionization in aqueous solution.

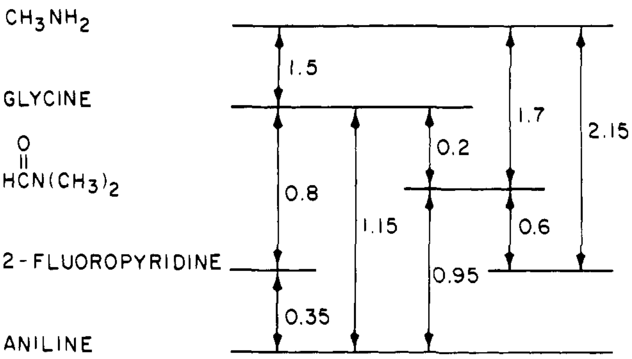


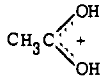
Figure 1. The basicity of the α-amino acid glycine in the gas phase relative to several reference bases previously studied by the equilibrium pulsed ICR technique. Each number listed is the result of a separate determination of $\Delta G_{382}°$ (kilocalories/mole) for proton transfer reactions such as $AH^+ + B = BH^+ + A$. The strongest base in this series is CH_3NH_2.

In this communication we report for the first time measurements of the gas-phase acidity and basicity of glycine. The experiments were performed with a specially constructed pulsed ion cyclotron resonance (ICR) spectrometer having a heated analyzer system. The procedures used to study the gaseous positive and negative ions of glycine were identical with those previously described in detail,[6] with the exception that the analyzer system was heated and the glycine sample was admitted to the spectrometer via a direct insertion probe. Each glycine sample was thoroughly dried to remove water. Electron impact ionization at 20 eV confirmed the presence of the base peak for glycine at *m/e* 30 and the absence of water. Under typical operating conditions of 109 °C, the pressure of glycine in the ICR analyzer cell was 1×10^{-6} Torr as measured by a Bayard-Alpert ionization gage.

Data for the equilibrium relative basicity of glycine in the gas phase are shown in Figure 1. Multiple determinations were made using four reference bases to ensure the reliability of the measurements. Glycine is found to be slightly less basic than methylamine. Based upon a value of 207.0 kcal/mol for the proton affinity of ammonia ($\Delta H_{298}°$ for $NH_4^+ = NH_3 + H^+$), the energetics for the gas-phase protonation reactions are as shown in reactions 3-5.[7] It is obvious from comparison of reaction 1 and reaction 3 that the basicity of glycine in the gas phase is enormously greater than in aqueous solution. This is primarily due to the high solvation energy of the proton. Of greater interest, however, is the finding that the gas-phase basicity of glycine is more similar to that of methylamine than acetic acid. We conclude from these data that in the gas phase glycine protonates on the α-amino group to produce the ionic structure shown in reaction 3.

$$H_3\overset{+}{N}CH_2COOH = H^+ + \text{glycine}, \quad \Delta G^\circ_{382} = 205.8 \text{ kcal/mol} \quad (3)$$

$$CH_3NH_3^+ = H^+ + CH_3NH_2, \quad \Delta G^\circ_{382} = 207.3 \text{ kcal/mol} \quad (4)$$



$$CH_3C(OH)_2^+ = H^+ + CH_3COOH, \quad \Delta G^\circ_{382} = 184.3 \text{ kcal/mol} \quad (5)$$

It has also been possible to measure the gas-phase acidity of glycine, and these data are shown in Figure 2. Glycine is a stronger acid than both acetic and formic acid in the gas phase. Based upon a value of 329.6 kcal/mol for the acidity of benzoic acid at 385 K, the energetics of the gas-phase deprotonation reactions are as shown in reactions 6-8.[8] It is apparent from reaction 6 that heterolytic bond dissociation, $AH = H^+ + A^-$, is a far more endothermic process in the gas phase than in aqueous solution (reaction 2). These data also show that gly-

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