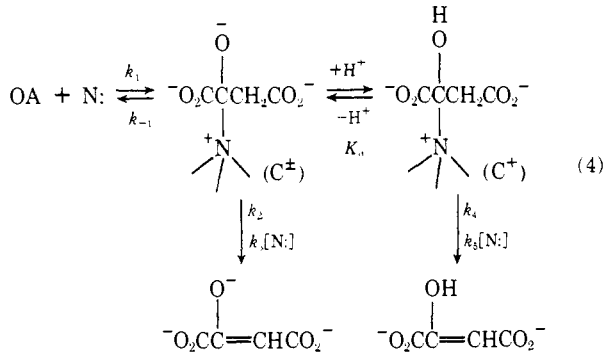
eq 3 are 0.26, 0.49, 1.9, 13, and 460 $M^{-1}$ $s^{-1}$ for $HPO_4^{2-}$, Im, $CO_3^{2-}$, $PO_4^{3-}$, and $HO^-$ giving a Bronsted $\beta$ of 0.35. A $-\alpha$ value of 0.43 is obtained for the general acid catalyzed mechanism of eq 2; the second-order rate constants are 1.4, 2.3, 11, and 9000 $M^{-1}$ $s^{-1}$ for $ImH^+$, $H_2PO_4^-$, pyridine-$H^+$, and $H_3O^+$, respectively.

More than general acid-base catalysis is involved in the catalysis of the enolization of OA by tertiary amines in water (30 °C, $\mu$ = 0.5).[8] Plots of $k_{obsd}$ vs total amine concentration ($[N]_T = [N:] + [NH^+]$) exhibit a break with $k_{obsd}$ becoming first order in $[N]_T$ at its higher values (Figure 2). Extrapolation of the upper portion of the curves, where $k_{obsd}$ is a linear function of $[N]_T$, to $[N]_T = 0$ provides intercepts which are from 25- to 500-fold greater (depending upon the pH) than the value of $k_{obsd}$ for enolization at the same pH but in the absence of amine and other buffer species.[9] This finding establishes that OA and tertiary amine form an intermediate species which yields enol on reaction with additional amine (the addition intermediate is required to be along the reaction path). The addition elimination mechanism of eq 4 is proposed.[10] At any con-



(4)

stant pH the mechanism of eq 4 prescribes (by assuming either steady-state or preequilibrium formation of $C^{\pm}$ and $C^+$) a rate equation of the mathematical form of eq 5. At

$$k_{obsd} = \frac{K_I[N]^2 + K_{II}[N]}{1 + K_{III}[N]} \quad (5)$$

values of [N] where the reaction becomes first order in this species (i.e., $K_{III}[N] > 1$), eq 6 pertains. In eq 6, $K_I/K_{III}$ =

$$k_{obsd} = \frac{K_I[N]}{K_{III}} + \frac{K_{II}}{K_{III}} \quad (6)$$

$k_1$ [steady state] or $(k_3K_a + k_5a_H)/(K_a + a_H)$ [preequilibrium formation of carbinolamines] while $K_{II}/K_{III}$ = $(k_1k_2K_a + k_4a_H)/(k_3K_a + k_5a_H)$ [steady state] or $(k_2K_a + k_4a_H)/(K_a + a_H)$ [preequilibrium]. Assuming preequilibrium formation of carbinolamine at high [N] and employing a $pK_a$ for $C^+$ of 11.3, determined by the $\rho_I$ method as used by Fox and Jencks,[11] the values of $k_3$ and $k_5$ may be calculated from the data of Figure 2 to be 151 ± 3 $M^{-1}$ $s^{-1}$ and 7.4 ± 3 $M^{-1}$ $s^{-1}$, respectively. Extrapolation of the linear portion of the plots of Figure 2 at high [N] to [N] = 0 (dashed lines in Figure 2) provides the term $K_{II}/K_{III}$ of eq 6. By employing $pK_a$ = 11.3 and the known pH, the values of $k_2$ and $k_4$ may be approximated as 22 ± 2 $s^{-1}$ and 0.70 ± 0.10 $s^{-1}$, respectively. These results establish that at high [N] the carbinolamines and ketone are in equilibrium and that the rate determining steps are amine ($k_3$ and $k_5$) and water catalyzed ($k_2$ and $k_4$) proton abstraction from carbinolamine. That $k_3 > k_5$ and $k_2 > k_4$ require that the negative charge on the carbinolamine oxygen provides considerable driving force for the elimination of amine. The details of the mechanism for the enolization of oxalacetate and its diethyl ester in the presence of oxyanion bases and tertiary amines will be given in a full paper.

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

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(8) Tertiary amines employed were quinuclidine, 3-quinuclidinol, 3-chloroquinuclidine, 3-quinuclidinone, trimethylamine, triethylamine, and pyridine. Of these only pyridine failed to act as a nucleophilic catalyst.
(9) Determined by employing a pH-stated spectrophotometric cell.
(10) In the reaction scheme of eq 4 amine catalyzed enolization of ketone has been ignored. Inclusion of this pathway provides a kinetic equation identical in form with that of eq 5. Most importantly, however, if amine catalysis through carbinolamine species is ignored and enolization of ketone by amine and/or lyate species is considered then a rate equation is obtained which does not accommodate the experimental results.
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## A $^{205}Tl$ Nuclear Magnetic Resonance Method of Determining Solvation Effects on Alkali Ion Selectivity

*Sir:*

The thallous ion has been proposed as a probe of the role of the alkali ions in biological systems[1-4] because its chemistry is like that of the alkali ions[5] and because of the comparative spectroscopic ease with which the thallous ion can be monitored. Two types of applications have been successful. One is the use of $Tl^+$ as a structural probe where the effect of a paramagnetic ion on the $Tl^+$ relaxation time is used to deduce the distance between the $Tl^+$ and the paramagnetic ion binding sites.[6,7] The other utilizes the quenching of $Tl^+$ luminescence upon complexation to determine the relative binding constants of the alkali ions through competition with the $Tl^+$.[8] Neither method yields information about the nature of the ligands comprising the binding site. The latter method is limited to methanol and water solutions because of the quenching of $Tl^+$ luminescence by most other solvents.[8]

We report here the use of the $Tl^+$ NMR chemical shift as a method which not only provides the relative binding constants of alkali ions but may also be useful in determining the type of donor atoms which comprise the binding site. The binding constants can be determined in a variety of solvents allowing the effect of ionic solvation on the ion selectivity to be measured. The chemical shift of the bound thallous ion is often diagnostic of the type of donor ligands involved in binding.[9,10]

The relative stability constants are calculated from eq 1.

$$K^M/K^{Tl} = \frac{P\{[I]_{tot} - (1-P)[Tl^+]_{tot}\}}{(1-P)\{[M^+]_{tot} - [I]_{tot} + (1-P)[Tl^+]_{tot}\}} \quad (1)$$

$[I]_{tot}$ and $[M^+]_{tot}$ are the total concentrations of ionophore and of added alkali ion, respectively. The population of uncomplexed $Tl^+$, $P$, is calculated from the chemical shift information as shown in eq 2.

Table I. Stability Constants of Alkali Metal Ion Complexes of the Crown Ethers Relative to that of $Tl^+$[a]

| Crown | Solvent[b] | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|---|---|
| DBC[c] | Methanol | 13.9 | 44.4 | 5.32 | 1.21 |
| | DMF | 6.29 | 15.5 | 2.82 | 0.752 |
| 18-Crown-6 | Methanol | 0.749 | 25.4 | 3.45 | 0.654 |
| | DMF | 0.054 | 2.33 | 1.44 | 1.00 |

[a] The uncertainty in the stability constant ratio is ±10%. [b] The anion in methanol is acetate; in DMF it is perchlorate. [c] Dibenzo-18-crown-6.

Table II. Chemical Shifts of $Tl^+$–Crown Ether Complexes and of Solvated $Tl^+$

| Crown | Solvent[a] | Calcd complexed ion shift | Calcd solvated ion shift | Exptl solvated ion shift |
|---|---|---|---|---|
| DBC[b] | Methanol | −35 | 497 | 512 |
| | DMF | −110 | 120 | 124 |
| 18-Crown-6 | Methanol | −70 | 500 | 512 |
| | DMF | −180 | 122 | 124 |

[a] Anion in methanol is acetate; in DMF it is perchlorate. [b] Dibenzo-18-crown-6.

$$P = (\delta - \delta_l)/(\delta_f - \delta_l) \quad (2)$$

$\delta$ is the chemical shift at the concentration of ionophore for which $P$ is being calculated, $\delta_l$ is the chemical shift of the $Tl^+$-ionophore complex, and $\delta_f$ is the shift of the free or uncomplexed $Tl^+$. The values of $\delta_l$ and $\delta_f$ are adjusted until the variance between the experimental chemical shifts and the chemical shifts calculated using the average stability constant ratio is minimized.

As an illustration of the method, the stability constants of alkali metal ion complexes of dibenzo-18-crown-6 (DBC) and 18-crown-6 relative to the stability constant of the $Tl^+$ complex are shown in Table I. The relative stability constants measured in methanol agree within experimental error with the relative values determined by Frensdorff using ion-selective potentiometry.[11] The selectivity sequence for DBC towards the alkali ions and $Tl^+$ in methanol is $K^+ > Na^+ > Rb^+ > Cs^+, Tl^+$. The same sequence is found in DMF which solvates better.[10] The selectivity sequence for 18-crown-6 in methanol is $K^+ > Rb^+ > Na^+, Cs^+, Tl^+$. The large difference in ionic radii between $Na^+$ and $Cs^+$ makes this sequence an excellent one to demonstrate solvent effects. When the selectivity sequence is determined in DMF, the more strongly solvated $Na^+$ has a significantly smaller relative stability constant than $Cs^+$ and the sequence becomes $K^+ > Rb^+ > Cs^+, Tl^+ > Na^+$.

The decrease in the relative stability constant of $Na^+$ over $Cs^+$ for 18-crown-6 with a change in solvent indicates that if a solvent of sufficient solvating ability were used for the determination of the DBC selectivity sequence, a decrease in the stability constant of $Na^+$ over $Rb^+$ should be found. This decrease was found in DMSO where the relative stability constants of the $Na^+$ and $Rb^+$ complexes of DBC are 5.60 ± 1.11 and 5.15 ± 0.59, respectively.

The calculated chemical shifts of the solvated ion and fully complexed ion are shown in Table II and compared to the measured shift of the solvated ion. The observed solvent dependence of the complexed ion shift occurs because the crown ether only occupies the equatorial coordination sites of the cation,[12,13] and an axial solvent or anion interaction can exist. The complexed ion shifts are in the proper region for ether type interactions (−80 to −170 ppm.). The $Tl^+$ shift is −80 ppm in THF, −130 ppm in dioxane, and −170 ppm in dimethoxyethane.[10]

The two major advantages of the Tl chemical shift method are the ability to measure solvation effects on the ion selectivity in a variety of solvents and the potential of determining the nature of the ligands comprising the binding site. The main disadvantage of this method as compared to the fluorescence method is the higher concentration of $Tl^+$ and therefore also of ligand that is necessary for measuring the relative stability constants.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this work.

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## On the Mechanism of a Rhodium-Complex-Catalyzed Carbonylation of Methanol to Acetic Acid

*Sir:*

Many rhodium compounds in conjunction with various forms of iodide have been reported[1] to catalyze the carbonylation of methanol to acetic acid. While it has been speculated[1b] on the basis of reaction rates and product distribution that various sources of rhodium and iodide may form the same active catalytic species, no direct evidence has been provided as to the specific nature of reactive intermediates either with any given catalyst precursor or with a variety of catalyst precursors. This work represents an attempt to define the various rhodium species present in the catalytic cycle when one particular compound, namely a rhodium(III) halide, is charged to the reaction as the catalyst precursor.[2] We present a pathway for the reaction which is consistent with the observed[1b] independence of the overall reaction rate on carbon monoxide pressure and methanol concentration.

It has been recognized[1b] that formation of a rhodium(I) species capable of oxidative addition of methyl iodide is an important part of any catalytic cycle for synthesis of acetic acid. The catalyst precursors chosen for study in this work, the rhodium(III) halides, react with carbon monoxide in hydroxylic media with excess halide to give the rhodium(I) species, $[Rh(CO)_2X_2]^-$.[3,4]

With this complex as the starting point we propose the reaction pathway illustrated in Scheme I.

The oxidative addition of alkyl halides to $d^8$ and $d^{10}$ complexes has been extensively studied recently.[5,6] Generally, addition simply results in formation of a metal-alkyl $\sigma$-bond. We find that when a solution containing $[Rh(CO)_2X_2]^-$ ions (with a variety of cations) reacts with excess methyl iodide at room temperature, the infrared