(eq 3). This observed rate equation is compatible with the

$$d[\mathbf{2}]/dt = (a + b/[\mathrm{PPh_3}])\,[\mathbf{2}] \qquad (3)$$

following formal rate expression (eq 4), which may be derived

$$d[\mathbf{2}]/dt = [k_1 + k_2K/[\mathrm{PPh_3}]]\,[\mathbf{2}] = k_{\mathrm{obsd}}[\mathbf{2}] \qquad (4)$$

from the following mechanism (eq 5) by assuming $K << [\mathrm{PPh_3}]$.

$$\mathrm{PdCOCOPh(Cl)(PPh_3)_2 \xrightarrow{k_1} PdCOPh(Cl)(PPh_3)_2 + CO}$$

$$\mathrm{PdCOCOPh(Cl)(PPh_3)_2 \overset{K}{\rightleftarrows} PdCOCOPh(Cl)(PPh_3) + PPh_3}$$

$$\mathrm{PdCOCOPh(Cl)(PPh_3) \xrightarrow{k_2} PdCOPh(Cl)(CO)(PPh_3)}$$

$$\mathrm{PdCOPh(Cl)(CO)(PPh_3) \xrightarrow[\text{fast}]{PPh_3} PdCOPh(Cl)(PPh_3)_2 + CO} \qquad (5)$$

A plot of k_{obsd} vs. $[\mathrm{PPh_3}]^{-1}$ allowed us to obtain k_1 and k_2K from the intercept and the slope, respectively. Analysis of the temperature dependence (17.1–34.2 °C) for the decomposition of **2** (Table I) yielded these values for the Arrhenius activation parameters: k_1, $E_a = 25.8 \pm 0.7$ kcal mol^{-1}, ln $A = 35.4 \pm 1.1$ ($\Delta H^{\ddagger} = 25.3 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = 9.74 \pm 0.37$ cal mol^{-1} K^{-1}); k_2K, $E_a = 31.7 \pm 0.6$ kcal mol^{-1}, ln A = 42.5 ± 1.0. Thus a significant pathway for the decarbonylation of **2** does not involve the prior dissociation of a ligand. This is in direct contrast to the behavior of the manganese compounds[8] which decarbonylate exclusively through a pathway involving prior ligand dissociation, presumbly because the latter are coordinatively saturated 18-electron complexes.

The rate of decarbonylation of **2** was unaffected at room temperature by the presence of CO up to a pressure of 700 psi. Similarly, no trace of **2** was observed when **1** was exposed to 1000 psi of CO at room temperature. These results indicated that the equilibrium constant for $\mathbf{1} + \mathrm{CO} \rightleftharpoons \mathbf{2}$ was extremely small at room temperature, and this observation together with the observed slow rate for the decarbonylation of **2** clearly showed that the rate of the reverse reaction, i.e., $\mathbf{1} + \mathrm{CO} \rightarrow \mathbf{2}$, must be negligible at room temperature under 15 psi of CO.

The reactions of **2** and **1** with $\mathrm{Et_2NH}$ are summarized below (eq 6–9). In light of these observations, we decided to react **2**

$$\mathbf{2} + \mathrm{Et_2NH} \xrightarrow[25\ ^\circ\mathrm{C,\ CH_2Cl_2}]{15\ \mathrm{psi\ CO}} \mathrm{PhCOCONEt_2} \qquad (6)$$

$$\mathbf{2} + \mathrm{Et_2NH} \xrightarrow[25\ ^\circ\mathrm{C,\ CH_2Cl_2}]{15\ \mathrm{psi\ N_2}} \mathrm{PhCOCONEt_2} \qquad (7)$$

$$\mathbf{1} + \mathrm{Et_2NH} \xrightarrow[25\ ^\circ\mathrm{C,\ CH_2Cl_2}]{15\ \mathrm{psi\ CO}} \mathrm{PhCOCONEt_2} \qquad (8)$$

$$\mathbf{1} + \mathrm{Et_2NH} \xrightarrow[25\ ^\circ\mathrm{C,\ CH_2Cl_2}]{15\ \mathrm{psi\ N_2}} \mathrm{PhCONEt_2}\ \text{(trace)} \qquad (9)$$

with $\mathrm{Et_2NH}$ in $\mathrm{CH_2Cl_2}$ at 25 °C while ^{13}CO was passed through the solution. If $\mathrm{PhCOCONEt_2}$ was formed by path A, no incorporation of ^{13}CO was expected. However, if **2** initially underwent CO deinsertion to the benzoyl species and subsequently formed $\mathrm{PhCOCONEt_2}$ through path B, then there should be significant incorporation of ^{13}CO next to the $\mathrm{NEt_2}$ group. This was based on the expected rapid exchange between the CO bound to the benzoyl species and the externally added ^{13}CO. The product observed was >96% $\mathrm{PhCO^{13}CONEt_2}$, as identified by GC–MS techniques. Furthermore, the observed fragments from the parent ion were $\mathrm{PhCO^+}$ and $\mathrm{^{13}CONEt_2^+}$. Thus we conclusively demonstrated that $\mathrm{PhCOCONEt_2}$ was formed from **2** and $\mathrm{Et_2NH}$ through path B. Clearly, therefore, the palladium-catalyzed "double carbonylation" reactions must also proceed through path B. The palladium-catalyzed formation of oxalates[11] and oxamides[12] from CO and alcohols or amines, respectively, presumably also proceeds through an analogous mechanism involving the direct attack of the nucleophile on two coordinated CO molecules to give species such as $\mathrm{Pd(CONuc)_2}$ which then undergoes reductive elimination to give the product. In a more general vein, our studies, together with the previously reported work on other systems,[8,13] indicate that a second insertion of CO into a metal acyl bond is an unfavorable step and is unlikely to occur in transition-metal-catalyzed carbonylation reactions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. This work was also partially supported by a grant from the Chevron Research Co. We also thank Johnson Matthey Inc. for a generous loan of palladium.

Registry No. 1, 50417-59-9; **2**, 88801-83-6; **3**, 88801-84-7; $\mathrm{Pd(PPh_3)_4}$, 14221-01-3; $\mathrm{Pt(PPh_3)_4}$, 14221-02-4; PhCOCOCl, 25726-04-9; $\mathrm{PhCOCONEt_2}$, 34906-86-0.

Supplementary Material Available: Plots of k_{obsd} vs. $[\mathrm{PPh_3}]^{-1}$ and ln k_1 vs. T^{-1} (2 pages). Ordering information is given on any current masthead page.

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Effect of Ionic Strength on Acid–Base Equilibria of Charged Ions in Highly Basic Media[1]

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Received December 9, 1983

The basicity scale H_{2-} has been introduced to describe acid–base equilibria involving deprotonation of monovalent anions in highly basic media.[3-5]

$$\mathrm{AH^- + OH^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} B^{2-} + H_2O} \qquad (1)$$

Because this scale is a modification of the H_- scale, which in effect extends the normal pH scale and was developed to describe the increased activity of $\mathrm{OH^-}$ at high base concentrations, one tends to consider H_{2-} as also referring to $\mathrm{OH^-}$ activity. Inspection of eq 1 shows that the rate constant of the forward reaction, but not that of the reverse, is expected to be ionic strength dependent. As a result the acid–base equilibrium constant $K = k_f/k_r$ should depend on ionic strength. In question are the magnitudes of the effect, particularly for equilibrium measurements on highly charged ions, and the significance of basicity scales such as H_{2-}. We demonstrate here that K for reaction 1 increases significantly with increased ionic strength. The H_{2-} basicity scale, as developed by Yagil,[4] effectively corrects measurements to zero ionic strength but is not uniquely defined by the base concentration alone. While basicity scales such as H_{2-} may be useful in empirical treatments of the concentration dependence of equilibrium data, they should not be interpreted as representing $\mathrm{OH^-}$ activity. Extension to scales suitable for use with more highly charged ions should be used with extreme caution.

The studies on which the above comments are based involve examination of deprotonation of carboxylated hydroxycyclohexadienyl radicals by ESR methods.[6] The experimental approaches are similar to those previously described.[7-10] The radicals

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[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2533 from the Notre Dame Radiation Laboratory.

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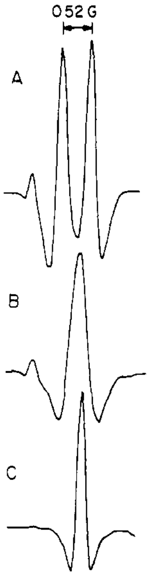

Figure 1. Structure of the low-field ESR "line" produced by splitting by H_6 in pentacarboxyhydroxycyclohexadienyl radical: A, 0.1 M KOH; B, 0.1 M KOH + 0.1 M Na_2SO_4; C, 0.1 M KOH + 0.5 M Na_2SO_4. In A additional splitting by the OH proton is observed showing that the rate of exchange with water is slow with respect to the frequency of the hyperfine interaction ($<10^7$ rad s^{-1}). The increased rate of exchange upon addition of sodium sulfate is directly demonstrated by the coalescence of this doublet into a single broad line in B, which is then narrowed in C. Line widths in A, B, and C are, respectively, 0.25, 0.44, and 0.20 G and are considerably greater than the limiting width of 0.11 G observed at both higher and lower base concentrations. The slight upfield shifts in the line centers in B and C correspond to decreases in a_{H_6} by 0.06 and 0.16 G and reflect increases in the equilibrium constant by factors of 3 and 9, respectively.

were produced by electron beam irradiation of N_2O-saturated basic solutions of carboxylated benzenes directly in the ESR cavity.[11] The radicals of interest resulted from OH addition. Sodium sulfate was used to increase ionic strength. At high base concentrations the ESR hyperfine constants represent the weighted average of the acidic and basic forms of the radical so that meaningful measurements can be made readily even if the radical represents only a minor component in the system. Hydroxycyclohexadienyl radicals are particularly suitable for probing basicity functions since their pK_a values are in the region above 13, and the proton hyperfine constant at C_6 is sensitive to the relative concentrations of the acidic and basic forms.[6]

The radicals chosen here to illustrate the effect of ionic strength were the OH adducts to 5-nitroisophthalic and benzenepentacarboxylic acids. In the latter case the effects on line shape at pH 13, illustrated in Figure 1, show dramatically that k_f increases with ionic strength. In the absence of sodium sulfate, splitting by the OH proton is still observed, showing that exchange with water is slow. Upon addition of 0.1 M sulfate the lines coalesce into a single broad line (width 0.44 G) which then narrows at higher sulfate concentrations. From the line widths pseudo-first-order rate constants of 0.4, 1.1, and 3.0 $\times 10^7$ s^{-1} are estimated. Simultaneously there are slight decreases in a_{H_6} (27.94, 27.88, and 27.76 G). Since a_{H_6} drops by $\sim$2 G on ionization,[6] these small differences correspond to increases in K by factors of $\sim$3 and 9. Thus k_r appears to be independent of ionic strength and is of the magnitude 3×10^9 s^{-1}. At 1 M KOH a_{H_6} decreases by 0.32 G on addition of 1 M sulfate, corresponding to an increase in K by only an additional factor of 2, about $^1/_2$ that expected from extrapolation of the above trend. The effect clearly approaches saturation so that an appropriate basicity scale will largely parallel H_- at high base concentrations.

Because its pK_a is lower ($\sim$13.5), the effect of increasing ionic strength on the OH adduct to 5-nitroisophthalic acid is considerably more pronounced. At pH 13 a_{H_6} decreases by 0.33 and 0.71 G upon addition of 0.1 and 0.5 M sulfate. When reflected on the base concentration dependence,[6] these decreases correspond to increases in K by factors of 1.4 and 1.8, respectively. While the effect of increasing ionic strength is substantial, it is considerably less than the factors of 4 and 80 expected from the low-concentration limiting law and slightly less than the factors of 1.5 and 2.1 suggested by extension of Yagil's arguments to doubly charged ions.

Major questions are apparent about the manner of treating equilibria involving charged ions in strongly basic media. Yagil's H_{2-} scale, in referencing measurements to zero ionic strength, is artificial in the sense that this scale does not correctly represent OH^- activity. On the basis of the above observations, we recommend that discussions be in terms of pH (H_- at high base concentrations) and that appropriate considerations be given to ionic strength effects. The present observations agree with Yagil's treatment in indicating that for ionic strengths (μ) less that 2 the correction term can be approximated as $n_-\mu^{1/2}/(1 + A\mu^{1/2})$, with n_- the ionic charge in the acidic form and A taken as 2.0. Above 2 M KOH this correction is somewhat less than the difference between Yagil's experimental H_{2-} and H_- scales. On what basis then does one compare acid–base equilibria measured at different ionic strength and for ions of different charge? If comparison is made after correction to zero ionic strength then the electrostatic energy will be important, but one is not usually interested in this aspect. It would appear better to make comparisons at high ionic strength where the effects of charge are minimized. In practical terms measurements made at base concentrations above 1 M will largely satisfy this criterion. In any event the basis on which the comparison is made should be stated clearly. Much more detail is, of course, needed, and it is clear that ESR measurements of the type reported here can give further insight. We are currently extending these investigations.

Acknowledgment. The authors thank Professor R. W. Fessenden and Dr. K. M. Madden for their assistance and discussions.

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Preparation and Spectral Characterization of Some Cyclic Acyl-1,1-diazenes

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Received June 17, 1983

Aminonitrenes or 1,1-diazenes, unlike the corresponding 1,2-diazene derivatives, are typically thermally unstable intermediates often used as in situ precursors of α,ω-biradicals.[1] Only recently Dervan and co-workers have succeeded in the preparation and spectral characterization of a number of persistent 1,1-diazenes,[2] which while stable enough for characterization in dilute solution rapidly decomposed below 0 °C. In spite of numerous synthetic and mechanistic studies presumably involving 1,1-diazenes as intermediates, very little experimental information is available on the effect of substituents on their thermal stability.[1,2] We now report the first spectral characterization of a number of sterically

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