Table I. Dediazoniation of 1 x 10^-4 M 16-ArN2+ in 0.01 M CTABr and 0.01 M HBr with Added BuOH at 40 °C. Normalized Product Yields of 16-ArOH, 16-ArBr, and 16-ArOBu*

<table>
<thead>
<tr>
<th>[BuOH]</th>
<th>% yield 16-ArOH</th>
<th>% yield 16-ArBr</th>
<th>% yield 16-ArOBu</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.000</td>
<td>72.9</td>
<td>27.1</td>
<td></td>
</tr>
<tr>
<td>0.100</td>
<td>75.6</td>
<td>22.6</td>
<td>1.8</td>
</tr>
<tr>
<td>0.219</td>
<td>78.9</td>
<td>18.2</td>
<td>3.0</td>
</tr>
<tr>
<td>0.437</td>
<td>83.5</td>
<td>11.8</td>
<td>4.6</td>
</tr>
<tr>
<td>0.656</td>
<td>87.0</td>
<td>7.3</td>
<td>5.8</td>
</tr>
<tr>
<td>0.765</td>
<td>88.0</td>
<td>5.7</td>
<td>6.3</td>
</tr>
<tr>
<td>0.874</td>
<td>88.5</td>
<td>4.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>

*Reaction is initiated by injection of 50 µL of 0.01 M 16-ArN2+ in MeCN into a 5-mL thermally equilibrated vial containing the needed reagents. After >10 half-lives (about 325 min), large aliquots are injected into the HPLC, overfilling the injector loop. Each HPLC peak area is measured, and calibration curves are in Table S1.

Our dediazoniation reaction is an excellent probe of association colloid interfaces. It distinguishes between chemically similar nucleophiles (e.g., Cl- and Br-; H2O and BuOH), and it can be used with all weakly basic nucleophiles which react by the same mechanism over a wide range of solution compositions. Future results should provide new information on the interfacial compositions of three- and four-component microemulsions.

Acknowledgment. We are grateful to C. A. Bunton, Fred Menger, and the reviewers for their helpful comments and to the following for financial support. The Busch and Biological Sciences Research Fund of Rutgers University, the donors of the Petroleum Research Fund, administered by the American Chemical Society (type G and type AC), Research Corporation, the National Institutes of Health (GM32972), and the NSF U.S.-Latin American Cooperative Program—Brazil.

Supplementary Material Available: Appendices S1 and S2, detailing dediazoniation salt preparation, dediazoniation kinetics, and the procedure for calculating interface concentrations of H2O, BuOH, and Br-; and Tables S1–S3, providing product yields and HPLC calibration data for dediazoniations of 16-ArN2+ and 16-ArN2+ (6 pages). Ordering information is given on any current masthead page.

Lithium Disopropylamide Mixed Aggregates: Structures and Consequences on the Stereochemistry of Ketone Enolate Formation

Angela S. Galano-Roth, Yong-Joo Kim, James H. Gilchrist, Aidan T. Harrison, David J. Fuller, and David B. Collum*

Department of Chemistry, Baker Laboratory Cornell University, Ithaca, New York 14853-1301

Received January 7, 1991

Stereochemical and regiochemical studies of ketone enolization by lithium dialkylamides have elicited extensive mechanistic discussions that typically invoke kinetic pathways in competition with enolate equilibriations. Noticeably absent from most (but not all) treatments are the possible roles of mixed aggregates and autocatalysis as determinants of selectivity and reactivity. Where

(4) Ketone enolate equilibration is often cited as the source of erosion of E/Z enolization selectivities. However, the measured rate of enolate equilibration appears to be too low: Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. J. Am. Chem. Soc. 1980, 102, 3959. More recent studies by Saunders and co-workers (7) and work in our laboratory (19) support a dominance of kinetic control even under high (Z)-enolate selective conditions.
(7) 16-ArN2+ is assumed to be completely microemulsion bound.
(8) It is water insoluble and more hydrophilic than CTABr; added BuOH reduces the cmc of CTABr, and the cmc of BuOH reduces the cmc of CTABr at 40 °C. CTABr's cmc = 1.08 x 10^-3 M in the absence of added salt.
(9) Table S1-S3 give product yields and calibration data for 16-ArN2+.
Due to the increasingly popular use of lithium amide/R,SiCl mixtures to effect lithiations,\textsuperscript{15} we investigated the influence of the LiCl generated in situ on the LDA solution structure. The \textsuperscript{6}Li NMR spectra of [\textsuperscript{6}Li,\textsuperscript{15}N]LDA/[\textsuperscript{6}Li]LiCl mixtures at low [LiCl] display a resonance corresponding to LDA along with a new doublet and triplet in a 2:1 ratio (Figure 1B).\textsuperscript{16} A single new \textsuperscript{15}N triplet of triplets in the \textsuperscript{15}N NMR spectrum indicating coupling to two inequivalent \textsuperscript{6}Li nuclei provides the additional information necessary to assign the mixed aggregate as a 2:1 LDA/LiCl mixed cyelic trimer.\textsuperscript{5} We hasten to add that the alternative ladder 6 is a potential structure possibility, which receives substantial support from lithium amide/lithium enolate mixed aggregate ladder structures.\textsuperscript{5,17} At higher [LiCl], one observes a new \textsuperscript{6}Li doublet (Figure 1C) and \textsuperscript{15}N quintet fully consistent with mixed dimer 7.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{\textbf{Figure 1} Spectra of lithium enolate/LDA mixed aggregates. (A) 6Li and \textsuperscript{15}N NMR spectra of [6Li,15N]LDA and two previously\textsuperscript{12} studied aggregates of free enolate. The corresponding \textsuperscript{15}N spectrum displays a new quintet along with the quintet of [6Li,\textsuperscript{15}N]LDA (6Li: spin 1/2). The multiplicities are fully consistent with formation of limited doublet indicative of coupling to one neighboring spin ISN (quintet.\textsuperscript{3})\textsuperscript{13} The corresponding \textsuperscript{15}N spectrum displays a new quintet along with the quintet of [6Li,\textsuperscript{15}N]LDA (6Li: spin 1). The multiplicities are fully consistent with formation of limited concentrations of mixed dimer 2. The (Z)-lithium enolate of pyrrolidine propionamide (3)\textsuperscript{11} affords limited concentrations of 1:1 mixed aggregate 4.\textsuperscript{4} In striking contrast, addition of 1.0 equiv of [\textsuperscript{6}Li][\textsuperscript{15}N]cyclohexenolate\textsuperscript{11} to [\textsuperscript{6}Li,\textsuperscript{15}N]LDA affords \textsuperscript{6}Li and \textsuperscript{15}N NMR spectra showing no evidence of a mixed aggregate.}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|c|}
\hline
Compound & Chemical Shift (\textsuperscript{6}Li) & Chemical Shift (\textsuperscript{15}N) \\
\hline
\textsuperscript{6}Li-enolate & 5.9 Hz, 1 Li & -0.15 ppm, minor, 0.62 ppm (d, J\textsubscript{L-N} = 4.9 Hz) \\
\textsuperscript{15}N-enolate & 5.9 Hz, 1 Li & -0.15 ppm, minor, 0.62 ppm (d, J\textsubscript{L-N} = 4.9 Hz) \\
\hline
\end{tabular}
\caption{Chemical shifts of lithium enolate/LDA mixed aggregates.}
\end{table}

Stereochmical studies on 3-pentanone enolization\textsuperscript{14} reveal possible consequences of mixed aggregation (eq 1). A slight decrease in E/Z selectivity is observed with increasing percent conversion, consistent with either partial enolate equilibration\textsuperscript{18} or the intervention of enolate/LDA mixed aggregates (Figure 2). Addition of pinacolone enolate or enolate 3 (0.1–2.0 equiv) prior to the addition of the 3-pentanone (0.9 equiv) produces minimal stereochmical changes. In contrast, LiCl shows a pronounced effect on the E/Z selectivity, with a sharp maximum in selectivity appearing at approximately 0.3 equiv (Figure 3). Whether this is a consequence of mixed aggregate based enolization or some form of electrophilic catalysis\textsuperscript{19} remains to be determined.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{\textbf{Figure 2} E/Z selectivity of 3-pentanone enolization. (A) 6Li NMR spectra of lithium enolate/LDA mixed aggregates. (B) \textsuperscript{15}N NMR spectra of lithium enolate/LDA mixed aggregates. (C) E/Z selectivity of 3-pentanone enolization.}
\end{figure}

In summary, the tendency of LDA to form mixed aggregates

\begin{equation}
\text{Me}_2\text{O} + \text{Me}_2\text{NC}l \rightarrow \text{Me}_2\text{OC}l \quad \text{LiCl}
\end{equation}


The \textsuperscript{6}Li-labeled enolates of pyrrolidine propionamide (3)\textsuperscript{11} affords limited concentrations of 1:1 mixed aggregate 4.\textsuperscript{4} In striking contrast, addition of 1.0 equiv of [\textsuperscript{6}Li][\textsuperscript{15}N]cyclohexenolate\textsuperscript{11} to [\textsuperscript{6}Li,\textsuperscript{15}N]LDA affords \textsuperscript{6}Li and \textsuperscript{15}N NMR spectra showing no evidence of a mixed aggregate.


[5] The \textsuperscript{6}Li-labeled enolates of pyrrolidine propionamide (3)\textsuperscript{11} affords limited concentrations of 1:1 mixed aggregate 4.\textsuperscript{4} In striking contrast, addition of 1.0 equiv of [\textsuperscript{6}Li][\textsuperscript{15}N]cyclohexenolate\textsuperscript{11} to [\textsuperscript{6}Li,\textsuperscript{15}N]LDA affords \textsuperscript{6}Li and \textsuperscript{15}N NMR spectra showing no evidence of a mixed aggregate.
Figure 1. \(^{6}\)Li NMR spectra of 0.1 M \([^{6}\text{Li},^{14}\text{N}]\text{LDA}\) in 3:1 THF/pentane at \(-115^\circ\text{C}\): (A) with 0.5 equiv of \([^{6}\text{Li}]\text{pinacolate}\); (B) with 0.4 equiv of \([^{6}\text{Li}]\text{LiCl}\); (C) with 1.5 equiv of \([^{6}\text{Li}]\text{LiCl}\). The spins of \(^{6}\text{Li}\) and \(^{14}\text{N}\) are 1 and \(1/2\), respectively.

Figure 2.

with ketone enolates is both limited and structure dependent, but the continuously changing proportions of LDA, lithium enolate, LDA/LiCl mixed aggregates are also observable and may have influence on lithium amides. Characteristics of this active-site complex include (i) a面条ity of three or four manganese atoms, (ii) a broad low-field parallel polarization mode EPR absorption (and (ii) a broad low-field parallel polarization mode EPR absorption.

Support for a Dimer of Di-\(\mu\)-oxo Dimers Model for the Photosystem II Manganese Aggregate. Synthesis and Properties of \([\text{Mn}_2\text{O}_2\text{)(tpmnn)}_2\text{)(ClO}_4\text{)}^+\]

Michael K. Chan and William H. Armstrong*

Department of Chemistry, University of California Berkeley, California 94720

Received July 12, 1990

The task of elucidating the structure of the manganese aggregate in the oxygen-evolving complex of Photosystem II (MnOEC), generally assumed to be the catalytic site of photosynthetic water oxidation, provides an interesting challenge for bioinorganic and biological chemists. Characteristics of this active-site complex include (i) a面条ity of three or four manganese atoms, (ii) a broad low-field parallel polarization mode EPR absorption (and (ii) a broad low-field parallel polarization mode EPR absorption.

Acknowledgment. We acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR02002), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility. We also thank the National Institutes of Health for direct support of this work.