The catalytic activity of the Rh compounds in olefin oxidational isomerization is largely determined by the HP structure, falling off in Rh(P(Ph)3)2COCl—HP systems in the order CHP > TBHP > 1-nonene hydroperoxide [3]. This ordering correlates well with the Rh(II) complex concentrations read from the ESR spectra. Thus introduction of CHP to a solution containing Rh(I) compounds gives rise to an ESR spectrum with Rh(II) lines whose intensity is high and increases rapidly with the passage of time. Addition of TBHP has the same effect, though the Rh(II) lines are less intense, and the intensity rises only slightly with the passage of time. An ESR signal for the Rh(II) complex could not be detected in the Rh(P(Ph)3)2COCl—CHP system. It is clear that a catalytically active Rh(II) complex is not formed here. This is consistent with the fact that Rh(P(Ph)3)2COCl does not catalyze olefin isomerization in the presence of CHP [3].

The authors would like to thank L. A. Blyumenfel'd for participation in a discussion of the results obtained in this work.

CONCLUSIONS

1. Paramagnetic Rh(II)O~ and Rh(II)RO 2" complexes of similar structure are formed in solutions containing triphenylphosphine Rh(I) complexes, both in the presence of O2 and in the presence of a hydroperoxide in an oxygen-free medium.

2. Addition of a hydroperoxide promotes coordination of the Rh(I) compound with both oxygen and RO2".

3. The Rh(II)RO 2" complexes coordinate olefins.

4. The effectiveness of the hydroperoxides in oxidational olefin isomerization can be correlated with the ability to oxidize Rh(I) to Rh(II).

LITERATURE CITED


KINETICS AND STOICHIOMETRY OF THE REACTION OF 2,2,6,6-TETRAMETHYLPIPERIDIN-1-OXYL WITH XENON DIFLUORIDE

V. A. Golubev, N. N. Salmina, B. L. Korsunskii, N. N. Aleinikov, and F. I. Dubovitskii

Nitroxy1 radicals are carried over to o xoammonium fluoride under the action of XeF2, a one-electron oxidizing agent [1]. This reaction follows a complex mechanism, yielding not only o xoammonium salts but...
TABLE 1. Stoichiometry of the Reaction of 2,2,6,6-Tetramethylpiperidin-1-oxyl with XeF₂

<table>
<thead>
<tr>
<th>T, °C</th>
<th>Solvent</th>
<th>[NO₃]₀</th>
<th>[XeF₂]₀</th>
<th>Δ[XeF₂]</th>
<th>Δ[NO₃]</th>
</tr>
</thead>
</table>
| 20    | H₂O     | 0.05   | 0.046  | 1.07±0.02
| 25    |        | 5.10⁻⁴ | 5.10⁻⁴ | 4.14±0.02
| 50    |        | 5.10⁻⁴ | 5.10⁻⁴ | 0.78±0.02
| -35   | MeCN    | 0.32   | 0.32   | 0.32±0.03
| 0     |        | 1.0    | 1.0    | 1.25±0.05
| 50    |        | 5.10⁻⁴ | 5.10⁻⁴ | 1.55±0.05
| 50    |        | 5.10⁻⁴ | 5.10⁻⁴ | 1.55±0.05

TABLE 2. Products from the Reaction of 2,2,6,6-Tetramethylpiperidin-1-oxyl with Xenon Difluoride

<table>
<thead>
<tr>
<th>Solvent</th>
<th>T, °C</th>
<th>[NO₃]₀</th>
<th>[XeF₂]₀</th>
<th>Δ[XeF₂]</th>
<th>Δ[NO₃]</th>
<th>Δ[NO]</th>
<th>Δ[NO]</th>
<th>Δ[NO]</th>
<th>Δ[NO]</th>
<th>Δ[NO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>21</td>
<td>5</td>
<td>4.6</td>
<td>1.0±0.05</td>
<td>0.42±0.02</td>
<td>0.42±0.02</td>
<td>0.42±0.02</td>
<td>0.42±0.02</td>
<td>0.42±0.02</td>
<td>0.42±0.02</td>
</tr>
<tr>
<td>H₂O</td>
<td>20</td>
<td>5</td>
<td>1.0</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
</tr>
<tr>
<td>MeCN</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
<td>1.2±0.1</td>
</tr>
<tr>
<td>MeCN</td>
<td>20</td>
<td>5</td>
<td>1.0</td>
<td>1.0±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
<td>0.5±0.05</td>
</tr>
</tbody>
</table>

other products as well. We have studied the kinetics and stoichiometry of nitroxyl radical oxidation for the special cases of the reaction of 2,2,6,6-tetramethylpiperidin-1-oxyl (I) with XeF₂

\[
\text{NO} + \text{XeF}_2 \rightarrow \text{NO} + \text{Xe} + \text{Products}
\]

EXPERIMENTAL

The kinetics and stoichiometry of the reaction of (I) with XeF₂ were studied in H₂O and CH₃CN where the rate of reaction is many times greater than the rate of hydrolysis. The stoichiometric coefficients were determined by carrying out the reaction with one of the components present in excess. The reaction was assumed to be completed when there was no further consumption of (I), or no further evolution of free Xe. The amount of evolved Xe was determined either volumetrically or manometrically. Since Xe is quite soluble in both water and CH₃CN, the accuracy of the volumetric measurements was increased by saturating the solutions with Xe prior to mixing. The manometric measurements were carried out in a thermostated quartz cell equipped with a planar membrane [2], correction being made for the solubility of Xe in CH₃CN, the latter proportional to the partial pressure of Xe.

The concentration of (I) was determined spectrophotometrically and by ESR methods [3]. The concentration of the 2,2,6,6-tetramethyl-1-oxopiperidinium cation (II) was determined spectrophotometrically [3], and by iodometric titration in acetic buffer [4]. The total concentration of (I), (II), and all other oxidizing agents was determined by iodometric titration in 1 N HCl or H₂SO₄. The F⁻ ion concentration was determined thorimetrically [5]. The (I) and (II) were freed of impurities which might interfere with this determination by boiling the sample taken for analysis with CH₃OH at pH ~0. The amount of product acid was determined by rapid potentiometric titration to the equivalence point at pH ~8.

The reaction rate was measured either in terms of the consumption of (I), following ESR methods, or in terms of the volume of liberated Xe, following manometric methods. Solutions were made up in deionized water with a specific conductance of 10⁻⁷ Ω⁻¹.cm⁻¹, or in spectrally pure CH₃CN with a transmission of better than 90% at λ 210 nm, measurement being at a layer depth of 1 cm.