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A Non-Radical Chain Mechanism for Oxygen Atom Transfer with a Thiorhenium(V) Catalyst

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The compound $\mathrm{MeRe(S)(mtp)(PPh_3)}$, **2**, where $\mathrm{mtpH_2}$ is 2-(mercaptomethyl)thiophenol, was used to catalyze the reaction between pyridine *N*-oxides, PyO, and triphenylphosphine. The rate law is $-\mathrm{d[PyO]}/\mathrm{d}t = k_c'[\mathbf{2}]\cdot[\mathrm{PyO}]^{1/2}$, with k_c' at 25.0 °C in benzene = 0.68 (4-picoline *N*-oxide) and 3.5×10^{-3} $\mathrm{dm^{3/2}\ mol^{-1/2}\ s^{-1}}$ (4-$\mathrm{NO_2}$-pyridine *N*-oxide). A chain mechanism with three steady-state thiorhenium species as chain carriers is implicated.

The specific reaction between 4-picoline *N*-oxide and triphenylphosphane, eq 1, has a substantial thermodynamic driving force:[1]

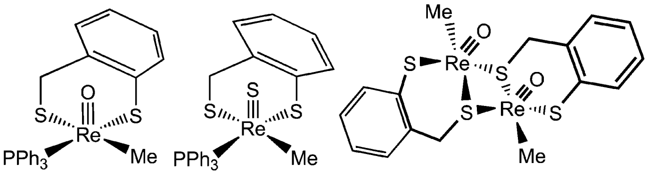
$$\text{4-PicO} + \mathrm{PPh_3} \rightarrow \text{4-Pic} + \mathrm{Ph_3PO}$$

$$\Delta H^\circ\ (\sim\Delta G^\circ) = -266\ \mathrm{kJ} \tag{1}$$

The easily prepared compound $\mathrm{MeReO(mtp)PPh_3}$, **1** in Chart 1, in which $\mathrm{mtpH_2}$ is 2-(mercaptomethyl)thiophenol, is a practical catalyst for gram-scale reactions under benchtop conditions.[2,3] Compound **1**[4,5] and other rhenium compounds[4,6] also catalyze oxygen atom transfer.

The reason for continuing this line of investigation is not to improve upon this or other[7] methods for the deoxygenation of *N*-heterocycles, but to gain further mechanistic insight.

Chart 1. Structural Formulas of Catalysts **1**−**3**



1 **2** **3**

Here, we report the results of an investigation of the thio analogue of **1**, $\mathrm{MeReS(mtp)PPh_3}$, **2**.[8] The rate laws for catalysts **1** and **2** have entirely different forms:

$$v = k_c[\mathbf{1}][\mathrm{PicO}]^2[\mathrm{PPh_3}]^{-1} \tag{2}$$

$$v = k_c'[\mathbf{2}][\mathrm{PicO}]^{1/2} \tag{3}$$

The first issue to be dealt with is the kinetic data and their mathematical analysis, especially the unusual half-order dependence. Such a form must be verified to hold over a wide concentration range of PicO. If not, then there is a substantial risk that the claimed half-order form is erroneous, perhaps the result of a kinetic study over a limited range. An apparent half-order dependence might, for example, result from the intermediate segment of a common kinetic saturation curve, $v = kC/(1 + \kappa C)$.

Two methods of data analysis were used to authenticate eq 3. In one, the order was derived from a plot of log v_i (initial reaction velocity) against log [PicO] over the concentration range 3.4×10^{-6} to 5.1×10^{-2} mol $\mathrm{dm^{-3}}$ of PicO, a factor $>10^4$. To attain this wide range of [PicO], both ^{1}H NMR and UV−vis methods were used for kinetics. Figure 1 presents the log−log plot, which is linear with a slope (i.e., the order with respect to [PicO]) of 0.53 ± 0.01. The ordinate displays $v_i/[\mathbf{2}]$, rather than v_i, thus normalizing the rates to unit catalyst concentration.

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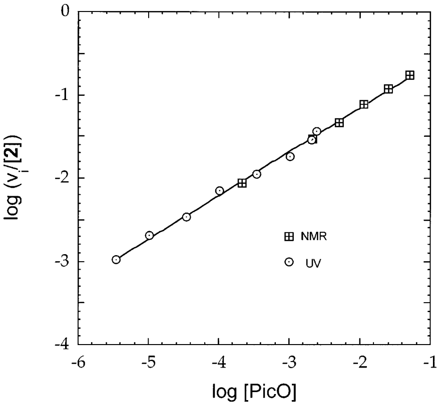


Figure 1. Dependence of the initial rate in benzene at 25.0 °C on the initial concentration of 4-picoline shown in the form of a log−log plot. In these experiments, [**2**] was $2.3-3.7 \times 10^{-5}$ mol L^{-1} and [PPh$_3$] $\geq 3.5 \times 10^{-3}$ mol L^{-1}. The least-squares slope of the line is 0.53 ± 0.01, which represents the order with respect to [PicO].

In the other method, data taken over the full time-course of the reaction with ^{1}H NMR spectroscopy were recorded. This approach allowed the identities and concentrations of reactants and products to be determined as a function of time. Pseudo-half-order rate constants k were determined by fitting the concentrations of PicO to this equation:[9]

$$[\mathrm{PicO}]_\mathrm{t} = \left(\sqrt{[\mathrm{PicO}]_0} - \frac{kt}{2}\right) \qquad (4)$$

The rate constants from both methods agreed well. For the two substrates studied, the rate constants in benzene at 25.0 °C are $k'_\mathrm{c} = k/[\mathbf{2}] = 0.68 \pm 0.02$ (4-PicO) and $(3.5 \pm 0.1) \times 10^{-3}$ dm$^{3/2}$ mol$^{-1/2}$ s^{-1} (4-NO$_2$-PyO).

Equation 3 with **2** as the catalyst can best be interpreted in terms of a chain mechanism, in which *at least* two (three, in this case) intermediates cycle in the propagation steps. Chains are terminated when two of the intermediates annihilate one another, re-forming stable thiorhenium(V) species **2**. Indeed, one can hardly envisage a nonchain scheme because the transition state cannot contain a half-molecule of PicO.[10] Two intertwined factors are devising a set of reactions that leads to the correct kinetic form, and proposing the chemical forms of reaction intermediates that can plausibly react as required.

To make the analysis easier to follow, however, it seems best to separate these issues. Scheme 1 presents in symbolic form what appears to be the *minimum* reaction set, in accord with Occam's Razor.

The kinetic derivation for Scheme 1 follows from the steady-state (ss) approximation for the concentrations of the intermediates, which is valid because only the parent catalyst **2** could be detected by ^{1}H NMR during catalytic turnover: $[\mathbf{2}] \gg \sum([\mathbf{I_i}])$. Consequently,[11]

$$k_\mathrm{init}[\mathbf{2}][\mathrm{MeReS(mtp)OPy}] = k_\mathrm{term}[\mathbf{I_1}][\mathbf{I_2}] \qquad (5)$$

$$k_1^\mathrm{prop}[\mathbf{I_1}][\mathrm{PPh_3}] = k_2^\mathrm{prop}[\mathbf{I_2}] = k_3^\mathrm{prop}[\mathbf{I_3}][\mathrm{PyO}] \qquad (6)$$

Scheme 1. Proposed Chain Reaction Scheme

$$\mathbf{2} + \mathrm{PyO} = \mathbf{I_4}\ [\mathrm{MeReS(mtp)(OPy)}] + \mathrm{PPh_3}\quad (\boldsymbol{K_1})$$

$$\mathbf{2} + \mathbf{I_4} \rightarrow \mathbf{I_1} + \mathbf{I_2}\quad (k_\mathrm{init})$$

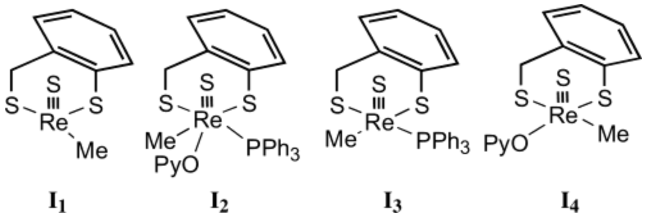
$$\mathbf{I_1} + \mathrm{PPh_3} \rightarrow \mathbf{I_3}\quad (k_1^\mathrm{prop})$$

$$\mathbf{I_2} \rightarrow \mathbf{I_1} + \mathrm{Ph_3PO} + \mathrm{Py}\quad (k_2^\mathrm{prop})$$

$$\mathbf{I_3} + \mathrm{PyO} \rightarrow \mathbf{I_2}\quad (k_3^\mathrm{prop})$$

$$\mathbf{I_1} + \mathbf{I_2} \rightarrow \mathbf{2} + \mathbf{I_4}\quad (k_\mathrm{term})$$

Chart 2. Structures Suggested for the Reaction Intermediates



Simultaneous solution of these equations gives the ss concentration of each intermediate under the assumption of long kinetic chains.[12] For example, $[\mathbf{I_1}]_\mathrm{ss}$ is

$$[\mathbf{I_1}]_\mathrm{ss} = \sqrt{\frac{K_1 k_\mathrm{init} k_2^\mathrm{prop}}{k_\mathrm{term} k_1^\mathrm{prop}} \frac{[\mathbf{2}]^2[\mathrm{PyO}]}{[\mathrm{PPh_3}]^2}} \qquad (7)$$

from which the net rate of the overall reaction 1 is given by eq 8, which agrees in form with eq 3, and so gains validity. The experimental rate constant k_c' is a composite of constants from Scheme 1.

$$v = k_1^\mathrm{prop}[\mathbf{I_1}]_\mathrm{ss}[\mathrm{PPh_3}] = \sqrt{\frac{K_1 k_\mathrm{init} k_1^\mathrm{prop} k_2^\mathrm{prop}}{k_\mathrm{term}}}[\mathbf{2}][\mathrm{PyO}]^{1/2} \qquad (8)$$

Chart 2 presents postulated structures, which for the time being will be taken as correct. Issues of chemical structure and reactivity will now be addressed. The initial step interconverting **2** and **I$_4$** is an equilibrium accompanied by geometrical isomerization. The reaction has been well-documented for oxo complex **1**,[13] where L represents a ligand such as a phosphane, pyridine, or thioether: $\mathrm{L_a}$ + *cis*(Me,ArS$^-$)-**1** = $\mathrm{L_b}$ + *trans*(Me,ArS$^-$)-[MeReO(mtp)L$_\mathrm{a}$]. Equilibrium in this step is by no means rapidly established,

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[9] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; pp 28−29.

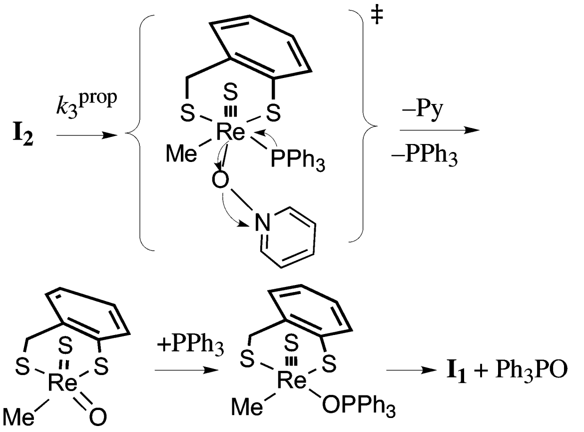
[10] The rate law for a chain reaction will not necessarily give the transition state composition, and usually will not, because of the relationships among the rates of the initiation, propagation, and termination steps in the mathematical analysis to obtain the rate equation for the overall reaction.

[11] The ss approximation, $\mathrm{d}[\mathbf{I_i}]/\mathrm{d}t = 0$, in a chain reaction leads immediately to certain useful relationships among the rates (not rate constants) of the constituent steps. The rates of initiation and termination are equal, as are the rates of the n propagation steps. With greater mathematical effort, one derives the ss rate law by simultaneously solving the three ss equations. For further detail, consult ref 9, pp 181−189.

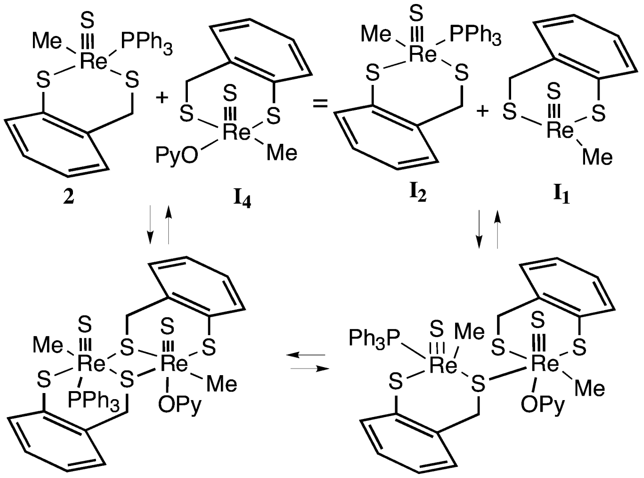
[12] Provided $v^\mathrm{prop} \gg v_\mathrm{init}$ (which means that the catalytic turnovers are high; in chain reactions this is called the long-chain approximation), the net reaction rate is essentially equal to the rate of any propagation step. Moreover, the summation of the chemical propagation steps gives the net reaction to an excellent approximation. This is clearly so here.

[13] Lahti, D. W.; Espenson, J. H. *J. Am. Chem. Soc.* **2001**, *123*, 6014−6024.

Scheme 2. The Third Propagation Reaction in Detail



Scheme 3. The Initiation/Termination Step



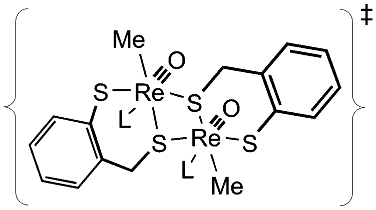
however, and it poses a substantial kinetic barrier for **1** and, we presume, for **2** as well.

The first propagation step is ligand addition to four-coordinate $\mathbf{I_1}$. A trapping experiment for $\mathbf{I_1}$ was carried out with 2,2′-bipyridine. A substantial concentration of bpy, ca. 0.2 mol dm^{-3}, significantly slows the reaction. Control experiments in the same reaction catalyzed by **1**, where no such intermediate intervenes, showed that 2,2′-bipyridine did not lower the rate; indeed, there was a small increase because bpy assists the reaction through its nucleophilic effect.

Rate constant k_3^{prop} will be large because the product $\mathbf{I_3}$ is five-coordinate. $\mathbf{I_3}$ is, of course, the geometric isomer of **2**, the latter much favored by thermodynamics. The interconversion of such isomers is *never* unimolecular (from Re−oxo data); displacement of one ligand by another is required. When the ligands are phosphanes, the reactions (again, relying on Re−oxo) are slow;[13] they remain unimportant here. The third propagation step is ligand addition trans to the oxo group. The resulting six-coordinate species is unstable with respect to further reaction, as given by the second propagation step, which is shown in Scheme 1 as a single reaction, which suffices for the kinetic analysis, but (again, from Re−oxo chemistry) is more likely the sequence presented in Scheme 2. Note the nucleophilic role triphenylphosphine plays in the transition state in Scheme 2. This chemistry presents a close parallel to nucleophilic assistance in oxygen atom transfer reactions with **1**[3] and **3**[14] as catalysts.

The initiation−termination step poses other issues. On first examination, it appears unprecedented. There does appear to be a relation to the well-studied reaction, **3** + 2L (L = phosphine, pyridine, thioether, etc.) = 2 [MeReO(mtp)L],[15] which occurs predominantly at a rate given by eq 9, with a transition state as depicted:

$$-\mathrm{d}[\mathbf{3}]/\mathrm{d}t = k[\mathbf{3}][\mathrm{L}]^2 \tag{9}$$



With that in mind, consider a mechanism for the initiation/termination step, $\mathbf{2} + \mathbf{I_4} = \mathbf{I_2} + \mathbf{I_1}$. Scheme 3 presents the mechanism that we suggest. It has been drawn with the participants arranged to facilitate comparison among the monorhenium reactants and products and the suggested dirhenium intermediates.

In conclusion, this work reports a reaction with a remarkable rate law. A chain reaction scheme can account for the kinetics. There are reasonable chemical interpretations for the reactions and proposed intermediates. This includes the nucleophilic assistance presented in Scheme 2, which has been reported previously when **1** or **3** is the catalyst, and the initiation and termination reaction between two rhenium(V) compounds, as in Scheme 3.[16]

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(16) The reaction progress was monitored spectrophotometrically where the pyridine *N*-oxides absorb strongly: PicO, $\epsilon_{330} = 945$ dm^3 mol^{-1} cm^{-1}; 4-NO$_2$PyO, $\epsilon_{352} = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}. The concentration of **2** was also monitored at its CT band, $\epsilon_{514} = 1.34 \times 10^3$ dm^3 mol^{-1} cm^{-1}. The characteristic ^{31}P chemical shifts, δ, in C$_6$D$_6$ are **2**, 22.8; PPh$_3$, −4.4; Ph$_3$PO, 25.7; Ph$_3$PS, 43.6; and **1**, 27.8. Both NMR and UV/vis measurements were used to show that during the time scale over which reaction 1 was catalyzed by **2**, the catalyst did not change form. Over longer times, however, **2** is not indefinitely stable in benzene, even without other reagents. Compound **2** also reacts slowly with PyO, Py, and traces of water in benzene, the latter especially when PPh$_3$ is present.