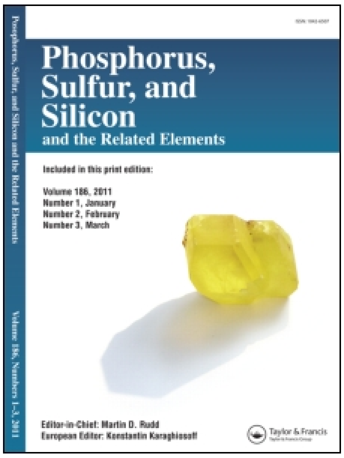

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ATOM TRANSFER AND EXCHANGE REACTIONS INVOLVING OXYGEN, SULFUR AND SELENIUM

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A systematic comparison has been made of the reaction conditions required to bring about the thermal transfer or exchange of Group 16 terminal elements between Group 15 molecular centers. Where reaction conditions were suitable, kinetic analyses have been performed, with the observed second-order behavior supporting the presumed bimolecular character of these reactions.

Key words: Oxygen transfer; sulfur transfer; selenium transfer; exchange; redistribution.

INTRODUCTION

Atom transfer reactions, particularly those involving the transfer of a Group 16 element between two molecular centers, have been observed previously in a variety of systems. There have been reports, for example, of oxygen transfer to phosphorus from nitrogen,[1] arsenic,[2] sulfur,[3] and selenium[4] centers. Similarly, the transfer of sulfur from sulfur[5] or phosphorus[6] centers, and the transfer of selenium from phosphorus[7] or arsenic[8] centers have been reported. Such reports have generally been isolated observations, however, and there has been no systematic investigation which compares the facility of these reactions in diverse systems. The present study features such a comparative examination, focusing on the thermal transfer of a Group 16 element (oxygen, sulfur or selenium) between two Group 15 centers, with phosphorus, arsenic or antimony serving as the donor element and phosphorus or arsenic as the acceptor element. In addition to establishing Periodic trends in reactivity for these simple atom transfer reactions, a direct comparison of reaction conditions has been achieved for the first time between simple atom transfer and mutual atom exchange.

RESULTS AND DISCUSSION

$$\mathrm{Ph_3M{=}X + Ph_2MeL \rightleftarrows Ph_3M + Ph_2MeL{=}X} \qquad \textbf{(A)}$$

$$\mathrm{Ph_3M{=}X + Ph_2MeL{=}Y \rightleftarrows Ph_3M{=}Y + Ph_2MeL{=}X} \qquad \textbf{(B)}$$

$\mathrm{Ph = C_6H_5}$, $\mathrm{Me = CH_3}$, $\mathrm{M = P, As, Sb}$, $\mathrm{L = P, As}$, $\mathrm{X/Y = O, S, Se}$

Reactions **A** and **B** depict the atom transfer and exchange reactions, respectively, for the actual systems examined in this study. For simplicity, the Group 15

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centers were restricted to either triphenyl or diphenylmethyl ligands. Both the transfer (**A**) and exchange (**B**) processes were examined under identical reaction conditions. Each reaction system consisted initially of an equimolar mixture of the two reactant species. These were each present at a concentration of 0.070 Molar in bromobenzene, as the reaction solvent. The reaction mixtures were prepared under nitrogen in NMR sample tubes; for the reactions requiring elevated temperatures, the samples were sealed under vacuum. The progress of each reaction was readily monitored by ^{1}H-NMR spectroscopy, using the relative intensities of the reactant and product methyl signals, which were well-resolved for each of the reaction systems. Each reaction was monitored until it progressed to completion or a definite equilibrium mixture was attained. With one exception (noted below), the reactions occurred cleanly, with no spectral evidence of interfering processes or thermal decomposition. Where reaction conditions were favorable, complete kinetic analyses were performed, by heating the samples for measured time intervals in a thermostated oil bath. These reactions exhibited clean second-order kinetics, consistent with the bimolecular mechanism presumed to be in operation. For reactions in which an equilibrium is established and an equilibrium constant (K_{eq}) can be measured, a modified form of the second-order kinetics expression,[9] suitable for reversible reactions, was employed in order to obtain the rate constants (k).

The principal results of these studies are summarized in Table I. A number of general conclusions can be drawn from these results. (1) Comparison of reactions **1**, **5** and **10**, which involve atom transfer between two phosphorus centers, confirms that the facility of these reactions increases dramatically as one progresses from oxygen to sulfur to selenium, as the atom undergoing transfer. (2) Comparison of reactions **5**, **6** and **7**, which involve transfer of sulfur to a phosphorus center, illustrate how the *donor* ability of the Group 15 element *increases* as one progresses from phosphorus to arsenic to antimony. In complementary fashion, examination of reactions **2** and **4**, or **6** and **8**, which compare oxygen or sulfur transfer, respectively, from an arsenic center, reveals how the *acceptor* reactivity of the Group 15 element *declines* as one moves from phosphorus to arsenic. (3) In another revealing comparison, examination of reactions **1** and **4**, or **5** and **8**, which involve transfer of oxygen and sulfur, respectively, between two identical Group 15 centers, demonstrates that the enhanced donor reactivity of arsenic (relative to phosphorus) more than compensates for its diminished acceptor reactivity. (4) It should also be noted that whenever an atom is being transferred between two identical elements, as in reactions **4**, **5**, **8** and **10**, there is a consistent energetic preference, worth between 1 and 2 kcal/mol, for the terminal element to reside on the center bearing the methyl ligand. (5) The activation energy requirements for the mutual atom exchange reaction are considerably more demanding than for the simple atom transfer. Although selenium, **10**, and sulfur, **5**, can be transferred between two phosphorus centers at 30° (rapidly) and 130° (slowly), respectively, their mutual exchange between phosphorus centers, **11**, is a slow process even at 200°. Likewise, although transfer of sulfur from arsenic, **6**, and selenium from phosphorus, **10**, are both rapid reactions at 30°, their mutual exchange, **12**, is a slow process at 135°. It is reasonable to presume that these exchange processes involve a cyclic transition state or intermediate, in which both Group 15 centers

TABLE I

Rate and equilibrium constants for atom transfer and exchange reactions

R × *n*#	*R* × *n* type	Reactants	Products	Temp °C	K_{eq}	$t_{1/2}$ min	*k* L mol^{-1} sec^{-1}
1[a]	O transfer P to P	$Ph_3P=O$ Ph_2MeP	Ph_3P $Ph_2MeP=O$	250	—	>30,000	—
2[b]	O transfer As to P	$Ph_3As=O$ Ph_2MeP	Ph_3As $Ph_2MeP=O$	135	>500	1170	1.9×10^{-4}
3[b,c]	O transfer Sb to P	$Ph_3Sb=O$ Ph_2MeP	Ph_3Sb $Ph_2MeP=O$	160	>500	1670	2.2×10^{-4}
4[d]	O transfer As to As	$Ph_3As=O$ Ph_2MeAs	Ph_3As $Ph_2MeAs=O$	200	>1	>1200	—
5	S transfer P to P	$Ph_3P=S$ Ph_2MeP	Ph_3P $Ph_2MeP=S$	130	12	530	1.9×10^{-4}
6[b,e]	S transfer As to P	$Ph_3As=S$ Ph_2MeP	Ph_3As $Ph_2MeP=S$	30	>500	<5	—
7[b,f]	S transfer Sb to P	$Ph_3Sb=S$ Ph_2MeP	Ph_3Sb $Ph_2MeP=S$	30	>500	<1	—
8[g]	S transfer As to As	$Ph_3As=S$ Ph_2MeAs	Ph_3As $Ph_2MeAs=S$	30	5.3	25	4.4×10^{-3}
9[b,f]	S transfer Sb to As	$Ph_3Sb=S$ Ph_2MeAs	Ph_3Sb $Ph_2MeAs=S$	30	>500	<1	—
10[f]	Se transfer P to P	$Ph_3P=Se$ Ph_2MeP	Ph_3P $Ph_2MeP=Se$	30	22	<2	—
11	S/Se exchange P to P	$Ph_3P=S$ $Ph_2MeP=Se$	$Ph_3P=Se$ $Ph_2MeP=S$	200	1.8	1800	—
12[b,h]	S/Se exchange P to As	$Ph_3As=S$ $Ph_2MeP=Se$	$(Ph_3As=Se)$ $Ph_2MeP=S$	135	>500	270	6.5×10^{-4}

[a] No significant reaction was observed after 50 hours at 250°.

[b] The reaction proceeds essentially to completion.

[c] Triphenyl antimony oxide appears to exist in solution in equilibrium with oligomeric forms which effectively inhibit its reactivity as an oxygen donor, rendering it, unexpectedly, less reactive than triphenyl arsine oxide. One indication of this complexity is that the second-order kinetic plot for this system exhibits a noticeable deviation from linearity, quite in contrast to the other reactions studied.

[d] An accurate determination of the equilibrium and rate constant was precluded for this reaction, because the product diphenylmethylarsine oxide undergoes a competing thermal decomposition at 200°.

[e] The reaction is complete within 15 minutes after the rapid mixing of the reactants.

[f] The reaction is complete within 3 minutes after the rapid mixing of the reactants.

[g] This reaction was monitored by maintaining the sample in the NMR probe at 30°.

[h] The product triphenylarsine selenide undergoes dissociation under these conditions, releasing triphenylarsine and elemental selenium.

attain a state of pentacoordination. In contrast, the more facile transfer reactions most likely involve a simple nucleophilic substitution at the Group 16 element.

The relative trends in reactivity summarized above are all consistent with the general understanding that the relevant covalent bond energies associated with these Group 15 and 16 elements diminish progressively as one moves from the lighter to the heavier elements. Further experiments will attempt to expand these reactions to an even broader array of elements.

EXPERIMENTAL

The phosphines (Ph_3P, Ph_2MeP), arsines (Ph_3As, Ph_2MeAs) and stibine (Ph_3Sb) employed in this study were commercially available. The phosphine oxides ($Ph_3P=O$, $Ph_2MeP=O$) and arsine oxides ($Ph_3As=O$, $Ph_2MeAs=O$) were prepared by oxidation of the corresponding phosphines and arsines

TABLE II

^{1}H-NMR spectral parameters for methyl signals in bromobenzene solution

Sample	δ(PPM)	^{PH}J (Hz)
Ph_2MeP	1.43	4
$Ph_2MeP{=}O$	1.67	13
$Ph_2MeP{=}S$	1.93	13
$Ph_2MeP{=}Se$	2.13	13
Ph_2MeAs	1.30	—
$Ph_2MeAs{=}O$	1.78	—
$Ph_2MeAs{=}S$	1.82	—

using *m*-chloroperbenzoic acid in methylene chloride at 0°. Triphenyl antimony oxide, obtained from Strem Chemicals, was dried under vacuum, since it is highly hydroscopic. The phosphine sulfides ($Ph_3P{=}S$, $Ph_2MeP{=}S$) were prepared by sulfurization of the phosphines using elemental sulfur in benzene at 25°. The arsine sulfides ($Ph_3As{=}S$, $Ph_2MeAs{=}S$) were prepared by treatment of the arsines with elemental sulfur in refluxing bromobenzene. The phosphine and arsine sulfides were purified by column chromatography on silica gel, eluting the products with chloroform. Triphenyl antimony sulfide was obtained from Strem Chemicals. The phosphine selenides ($Ph_3P{=}Se$, $Ph_2MeP{=}Se$) were prepared by reaction of the phosphines with elemental selenium in refluxing benzene. The purities of the oxides, sulfides and selenides were established by thin layer chromatography on silica-coated sheets. The solvent used for the reactions under study, bromobenzene, was distilled and deoxygenated prior to use. The ^{1}H-NMR spectra were recorded on a Varian EM-360A spectrometer. Spectral parameters for the methyl signals used in monitoring the reactions are provided in Table II. For kinetic studies, samples were maintained in a Haake FS-2 thermostated oil bath, with temperatures held to within ±0.2°C of reported values.

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