

Products and Kinetics of the Reaction of Monomeric Target Bis-(Acetylacetonato) Copper(II) with Transmetalator Bis-(Diethoxydithiophosphato) Zinc(II) in Methylene Chloride

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Received 14 April 2015; accepted 25 May 2015; published 28 May 2015

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Abstract

Reaction of bis-(acetylacetonato) copper(II) (A) with transmetalator $\text{Zn}((\text{EtO})_2\text{PS}_2)_2$ (B_2 ; Et = ethyl) in methylene chloride is a simple irreversible second-order process over a wide temperature range which is the first example of a second-order reaction of mononuclear target A with a transmetalator. The plots of k_{obsd} vs $[\text{A}]$ are linear, meaning that there is one A and one B_2 in the activated complex of the slowest reaction step. The slowest step is precursor formation on the basis that B_2 is an exceptionally weak complex. The product of the A/ B_2 reaction is the strong successor complex $\text{Zn}(\text{acac})_2 \cdot \text{Cu}(\text{ps})_2$. The data are compared with those for reactions of the same target (A) with S-methyle isopropylidenehydrazinecarbodithioate-carbodithioato-metal(II) complexes $\text{M}(\text{SN})_2$ ($\text{M}=\text{Ni}$ (C_1) and Zn (C_2)). The reaction is not like that of A with $\text{Ni}((\text{MeO})_2\text{PS}_2)_2$ (B_1 ; Me=methyl), because it is irreversible and also consistent with the measured lower relative thermodynamic stability of B_2 compared to B_1 .

Keywords

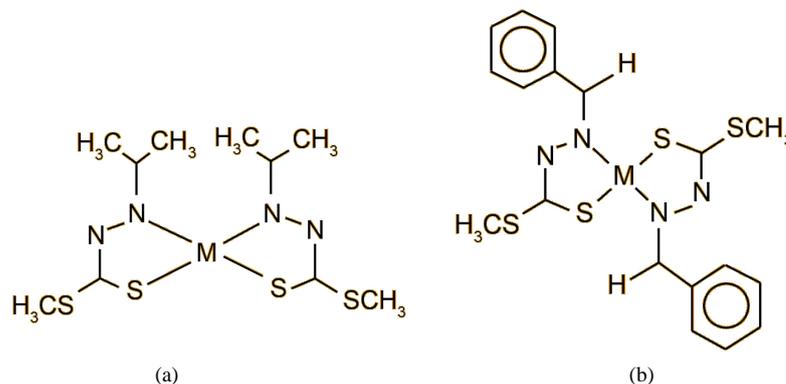
Kinetics, Mechanism, Transmetalation, Transmetalators, Thermodynamics

1. Introduction

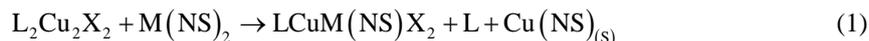
Transmetalation is the stoichiometric replacement of the metals in a polymetallic target with other metals from

How to cite this paper: Abo-Eldahab, H.A. (2015) Products and Kinetics of the Reaction of Monomeric Target Bis-(Acetylacetonato) Copper(II) with Transmetalator Bis-(Diethoxydithiophosphato) Zinc(II) in Methylene Chloride. *Open Journal of Physical Chemistry*, 5, 39-48. <http://dx.doi.org/10.4236/ojpc.2015.52005>

reagents called transmetalators [1]. It is a source of many new heteropolymetallic molecules that cannot be obtained by other means [2]. The transmetalation phenomenon has mostly been applied to polynuclear copper(I) [3]-[5] and copper(II) [1] [5]-[13] targets, although it is also applicable to targets containing other transition metals [10]. The best known transmetalators are S-methyl hydrazinecarbodithioate complexes $M(NS)_2$, where M is Co, Ni, Cu and Zn and NS is monoanionic S-methyl isopropylidenehydrazinecarbodithioate and S-methyl benzylidenehydrazinecarbodithioate in reagents a and b, respectively. Transmetalation reactions proceed under mild conditions in aprotic solvents and the heteropolymetallic products are easily separated [1] [2].



The major driving force for stoichiometric copper replacement is the formation of highly stable co-products $Cu(NS)_{(s)}$ and $Cu(NS)_2$ as typified by Equations (1) [5] and (2) [7], where the transmetalator is A; L is an N,N,N',N'-tetraalkyldiamine; N is a monodentate pyridine ligand and X is Cl or Br.



Extensive studies have shown that the patterns and specificity of progressive transmetalation reactions strongly depend on the target core structure [2].

Practical transmetalation reactions have the following characteristics:

1. The targets are easy to make and purify.
2. The reactions proceed at high rates under mild conditions in common solvents.
3. The products are in stoichiometric steps, as in Equation (3) with $x = 1 - 4$.



4. The desired heteropolymetallic products are easy to isolate.
5. They are characterizable solids that exist as members of families containing different metals M in different proportions.

Transmetalation chemistry is being developed and applied in four major areas:

1. The synthesis of heteropolymetallic molecule families as a means of understanding the structures of catalytic and non-catalytic homopolymetallic targets that decomposes on attempted crystallization. We have shown that transmetalation alters the rates and rate laws of copper-catalyzed reactions [1] [14] and gives valuable information about catalyst structures [15].

2. Application of the transmetalation phenomenon to unexplored elements. This requires new labile polymetallic targets and/or transmetalators containing the elements of interest. Until recently, transmetalation chemistry was restricted to the elements Fe [5], Co [8], Ni [1] [11], Cu [10], Zn [13] [16], Cd [14], Hg [14] and Sn [14] [17], because only these elements form useful transmetalators with excellent transmetalator ligand S-methyl isopropylidenehydrazinecarbodithioate (NS) [2]. However, we have now discovered that bis-(dialkoxydithiophosphato)-metal complexes $((RO)_2PS_2)_nM$ (abbreviated $M(PS)_n$) are transmetalators of copper targets. Application of transmetalation to new elements is likely to be successful because most of the metallic elements form dithiophosphato-complexes [18].

3. Thermal and electrochemical [17] [18] conversion of heteropolymetallic transmetalation products to bulk and supported metals, alloys and mixed metal oxides. The development of transmetalation chemistry thus goes hand in hand with new ways of making useful materials and catalysts.

4. Studies of transmetalation mechanisms. Transmetalation is remarkable because (a) direct transmetalation as in Equation (1) leaves the rest of the target unchanged [2] [3] [6] [7]; (b) targets react selectively with mixtures of transmetalators [8₆]; and (c) different metals in a heteropolymetallic target are specifically replaced: for example, Zn(NS) specifically replaces copper in targets $(\mu_4\text{-O})\text{N}_4\text{Cu}_{4-x}\text{M}_x\text{Cl}_6$ ($x = 1 - 4$) even though replacement of M also is thermodynamically favorable [9] [19]. This specifically has been traced kinetically to specific interaction of the transmetalator with the metal center that is replaced [20]. The interaction occurs in precursors $\text{TM}\cdot\text{T}_n$ through Equation (4), where TM is the transmetalator; T is the target, n is 1 or 2 and β_n can range from very small [22] to moderate and measurable [22] to very large [21] [22]. It also has been found that different forms of precursors with the same stoichiometry $\text{TM}\cdot\text{T}$ can exist in a given system at different temperatures [20]. However, the interaction is complicated by apparent involvement of more than one metal center of a polymetallic target with the transmetalator [20].



That is why we turned to bis-(acetylacetonato) copper(II) (A) as a model for the metal centers in polymetallic targets [22] [23]. Our work showed that:

1) A is capable of forming both moderately strong and very strong precursors ($n = 1$) Equation (4) with different $\text{M}(\text{NS})_n$ transmetalators) [22].

2) Different forms of $\text{TM}\cdot\text{T}$ precursors can be detected at different temperatures [22] [23] and the thermodynamic data can be correlated with data for precursor formation in irreversible polymetallic transmetalation systems [20]. This comparison shows that specific transmetalation occurs because:

Precursor formation is cooperative in the sense that no single property of T or TM determines the extent of precursor interaction or the rate of metal exchange [23].

3) The $\text{A}/\text{M}(\text{NS})_2$ systems are reversible, which enable us to compare the thermodynamics and other properties of precursor and successor complexes [22] [23].

4) Comparison of reaction profiles for irreversible and reversible $\text{A}/\text{M}(\text{NS})_2$ systems enables sub-classification of the systems according to the slow step (precursor formation thermodynamics, metal exchange kinetics and successor complex dissociation) [23].

With the promise of much new transmetalation chemistry based on $\text{M}(\text{PS})_n$ transmetalators on the horizon [18], though to provide a mechanistic comparison with established $\text{M}(\text{NS})_n$ transmetalation systems by studying the products and kinetics of reaction of target A with transmetalator $(\text{MeO})_2\text{PS}_2)_2\text{Ni}$ (B_1) [24]. The results show that:

1) the A/B_1 system is reversible and involves more stable reaction precursors $\text{A}\cdot\text{B}_1$ than the $\text{A}/\text{Ni}(\text{NS})_2$ (A/C) system [22] [25];

2) different precursors $\text{A}\cdot\text{B}_1$ and different successor complexes $\text{Ni}(\text{acac})_2\cdot\text{Cu}(\text{PS})_2$ exist at different temperatures;

3) the first thermodynamic data for precursors $\text{B}_1\cdot\text{A}_2$ ($n = 2$ in Equation (2)) can be obtained;

4) precursors, activated complex and successor complex formation involve much lower entropy changes in the A/B_1 system than in the A/C system.

2. Experimental

2.1. Materials

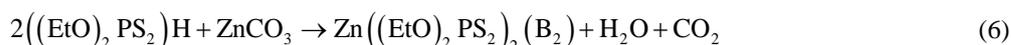
2.1.1. Target, Solvent and Reaction Environment

Bis-(acetylacetonato) copper(II) (A) (Alfa) was recrystallized from methylene chloride/diethylether. Methylene chloride was dried with H_2SO_4 , stirred with anhydrous sodium carbonate, freshly distilled from P_2O_5 and stored in the dark over anhydrous sodium carbonate. high purity dinitrogen was deoxygenated by passage through a freshly activated column of Alfa DE-OX catalyst.

2.1.2. Synthesis of Transmetalator, B_2

Bis(diethoxydithiophosphato) zinc(II) ($\text{Zn}(\text{PS})_2$, B_2) was synthesized by a modified form of the literature method [2]. B_2 thermally unstable and very air sensitive. It was therefore made at low temperature from reactions

Equations (5) and (6).



In a typical experiment, 12.7 gm P_4S_{10} (57.0 mmol) was placed in a 200 mL round-bottom flask fitted with a dinitrogen inlet, magnetic stirrer and reflux condenser. Deoxygenated anhydrous methanol (75 mL) was added and the mixture was refluxed under flowing dinitrogen until H_2S could no longer be detected in the effluent with lead acetate on damp filter paper (ca 45 min). At this point, $ZnCO_3$ (120 mmol) was added and the mixture was stirred under dinitrogen in the ice bath for 20 min. Pentane (50 mL) was then added and, after filtration, the filtrate was then pumped to dryness in a vacuum rotary evaporator. The white solid $Zn((EtO)_2PS_2)_2(B_2)$ obtained melts sharply at $74^\circ C$ and has a broad resonance in its ^{31}P NMR spectrum at 93.0 ppm.

2.1.3. Physical Measurements

Details of our procedures for product separation and analysis, kinetic measurements and data analysis can be found in the previous work [20]-[23] [26]. The relative thermodynamic stabilities of $Ni(PS)_2(B_1)$, $Zn(PS)_2(B_2)$, $Ni(NS)_2(C_1)$ and $Zn(NS)_2(C_2)$ in ethanol were established by visual inspection and spectrophotometric measurements following established procedures at room temperature.

The kinetic measurements were made with a DEC PRO380 computer-assisted Hi-Tech SFL41 stopped-flow spectrophotometer over the temperature range $-25.0^\circ C$ to $30.0^\circ C$ controlled to $\pm 0.05^\circ C$. The reaction of A with B_2 was monitored at 659 nm. The concentration ranges were $[A] = 2.50$ to 50.0 mM and $[B_2] = 0.50$ mM. All experiments with transmetalator $Zn(PS)_2(B_2)$ were conducted under dinitrogen. The concentration of A was always sufficient to ensure pseudo-first-order conditions. The pseudo-first-order rate constant k_{obsd} at fixed $[A]$, $[B]$, wavelength and temperature was obtained from the slope of a plot of $\ln(A_\infty - A_t)$, where A_t is the absorbance at time t. Each run was repeated at least three times to give a maximum error in each reported rate constant of $\pm 4\%$.

3. Results and Discussion

3.1. General Observation

Practical transmetalation reactions are irreversible and stoichiometric, proceed rapidly under mild conditions and give easily separated heteropolymetallic products. These considerations require that useful transmetalation systems have a large driving force and that the reactants be kinetically labile [2]. Polynuclear copper transmetalation targets that satisfy these requirements can contain bidentate N,N,N',N'-tetraalkylamine ligands L, Equation (7) [5] [21]



and even an anionic oxo-pyridine ligand that bridges the target metal centers [3] [4] [20]. The relative stabilities of transmetalators $M(NS)_2$ are useful guide to their relative reactivity's with a given target. Previous measurements show that $Cu(NS)_2$ is much more thermodynamically stable than transmetalation product $Ni(acac)_2$ [27].

3.2. Reactant Structures

Target A is a flat, neutral molecule [25] with only O-donor atoms. Reactant $Ni(PS)_2(B_1)$ is a diamagnetic, flat molecule with the CH_3O groups in a plane perpendicular to the N_1S_4 plane and a center of symmetry [25]. Reactant $Zn(PS)_2(B_2)$ is a diamagnetic, flat molecule with the C_2H_5O groups in a plane perpendicular to the N_1S_4 plane and a center of symmetry [25]. Transmetalator $Ni(NS)_2(C)$ is a flattened tetrahedron (the dihedral angle is 27°) with a *cis*-geometry [28]. The reactant core structures are shown in (Figure 1).

The essential differences between reactants B and C are as follows:

1) B contains four-membered rings while C contains five-membered rings. Electron delocalization in the rings of B is indicated by high sensitivity of the ^{31}P spectrum to the identity of M in $M(PS)_2$ [28].

2) Transmetalation requires the transfer of PS or NS ligands from the transmetalator metal to the target metal (see Equation (7)). Only M-S bonds have to be broken for this purpose in B, but the NS rings in C can, in prin-

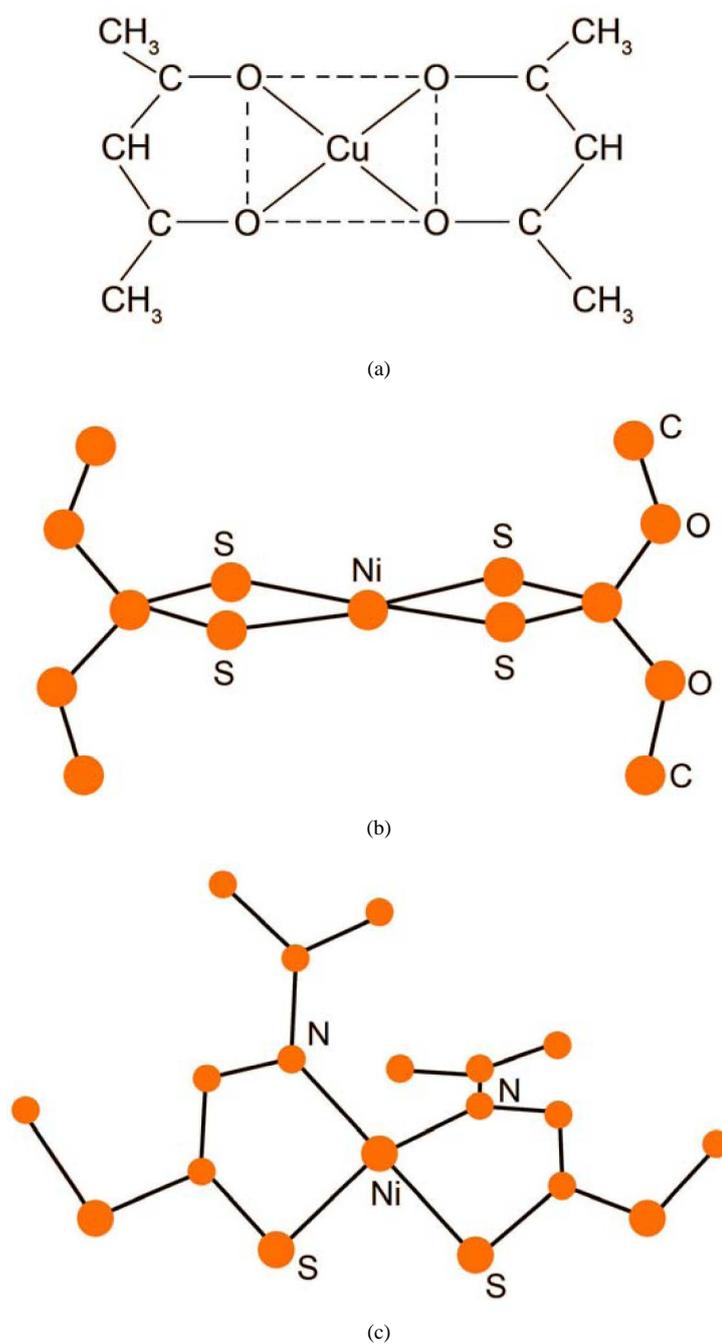


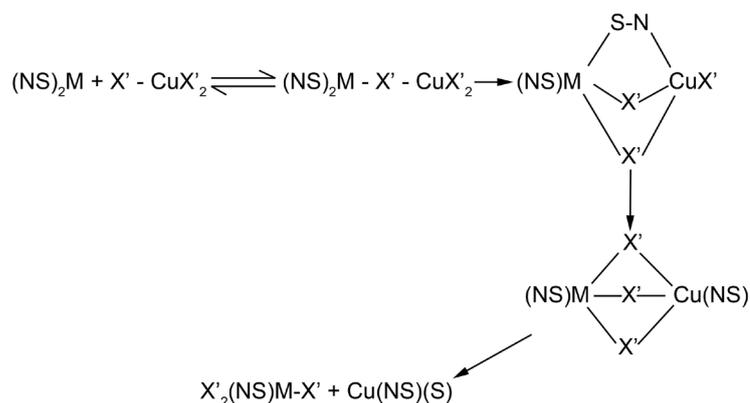
Figure 1. Core structures of target (a); reagent (b); and reagent (c).

ciple, open by Ni-N or Ni-S bond breaking.

3) Reactants B has much lower thermodynamic stability than reactant C [28].

3.3. Transmetalation Steps

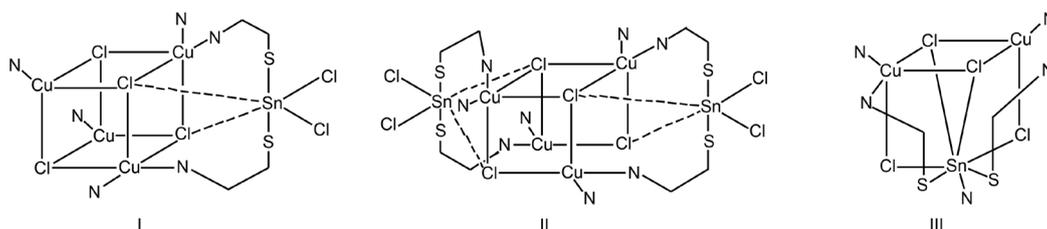
Our current view of the sequence of steps in transmetalation reactions is based on a great deal of kinetic information [22] [23] supplemented by very recent structural insights [18]. It is summarized in **Scheme 1**, where X are the outermost framework atoms of the copper target, M is the transmetalator metal and NS is the transmetalator ligand.



Scheme 1. The sequence of steps in transmetalation reactions.

The transmetalator metal M first interacts with the target atoms X. This increases the coordination number of M, whose NS chelate rings broken in this process and the freed N atoms are coordinated by the target metal center. The extent of this sharing of NS between M and the target metal determines the stoichiometry, strength and character of the precursors formed in Equation (2). The strength of M bonds to target X has now increased. The M-S bonds slowly break and the target metal chelates the transferring NS ligand. The final step is loss of Cu(NS)₂ from the original copper(II) target. The net result of transmetalation is the replacement of target metal-X bonds with M-X bonds.

This picture of transmetalation is supported by proof of the existence of precursor structures I and II in the reaction of Sn(NS)₂Cl₂ with target [NCuCl]₄ (N is N,N-diethylnicotinamide) and the isolation of product III from reaction of equimolar Sn(NS)₄ with the same target [19].



3.4. Kinetics of the Reaction of Cu(acac)₂, (A) with Zn((EtO)₂PS₂)₂, (B₂) in Methylene Chloride

Zinc transmetalator, B₂ is much less thermodynamically stable than nickel transmetalator, B₁ so we should expect B₂ to react more rapidly than B₁ with a target like A. This is borne out by the experimental data, which are collected in Table 1. The reaction of A with B₂ is a second-order, irreversible process, as demonstrated in Figure 2. The order is the same over a wide temperature range, as demonstrated by the linear plot in Figure 3.

3.5. Interpretation of the Data and Comparison with Other Second-Order Transmetalation Systems

Although many polymetallic target transmetalation reactions are second-order [20] [21], this is the first example of a second-order reaction of mononuclear target A with a transmetalator. The other systems either saturate or proceed at rates which are independent of target concentration [A] [22] [23].

3.6. There Are Two Important Characteristics of the A/B₂ System

First, the plots of k_{obsd} vs [A] are linear, which means that there is one A and one B₂ in the activated complex for the slowest reaction step. At the same time, this linearity indicates that the slow step does not involve significant

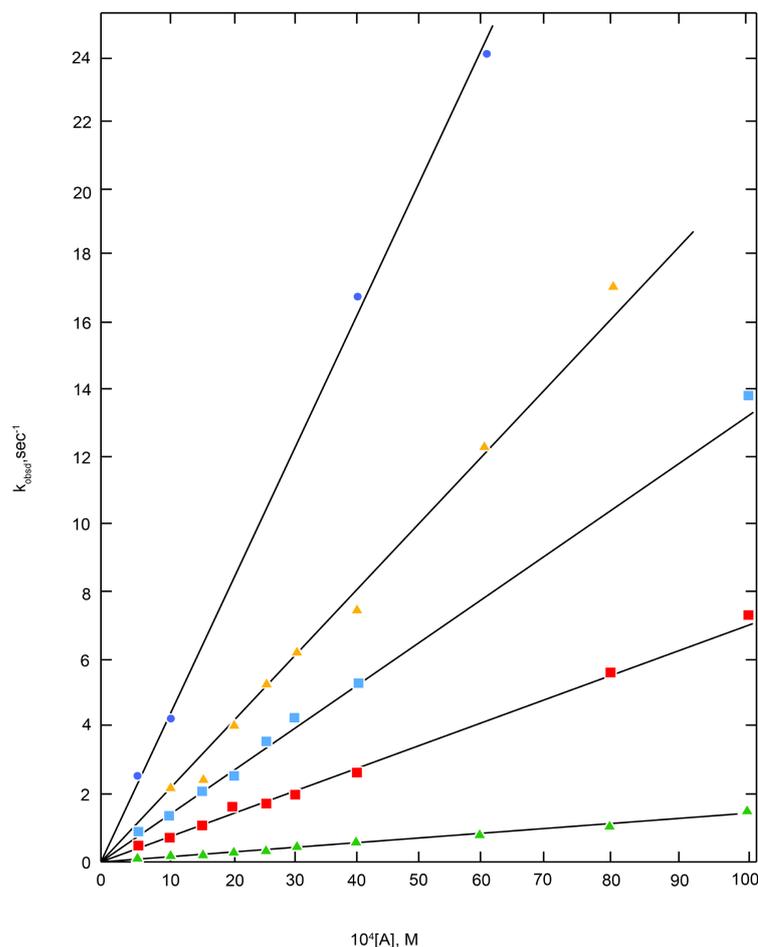


Figure 2. Plots of k_{obsd} vs $[A]$ for the reaction of A with $\text{Zn}(\text{PS})_2 \text{ B}_2$ in methylene chloride at the following temperatures ($^{\circ}\text{C}$).

Table 1. Kinetic data for the reaction of target A with $\text{Zn}(\text{PS})_2 \text{ B}_2$ in methylene chloride.

Temperature	$10^{-2}k_2, \text{M}^{-1}\text{sec}^{-1}$	$\Delta H_2^{\#a}$	$\Delta S_2^{\#b}$
-25.0	1.4		
-9.0	6.9		
0.0	12.6	10.7 ± 0.4	5 ± 5
10.0	21.4		
20.0	39.8		

^aUnits are kcalmol^{-1} ; ^bUnits are $\text{caldeg}^{-1}\text{mol}^{-1}$ at 25.0°C .

proportions of reaction precursors $A \cdot B_2$. Thus, the slow step is either precursor formation followed by very rapid metal exchange or slow metal exchange proceeding through a very weak precursor.

Second, the reaction is not like that of A with B_1 because it is irreversible. $\text{Zn}(\text{PS})_2 \text{ B}_2$ is one of the very least stable $\text{M}(\text{PS})_2$ complexes, so this is not too surprising because the product of the A/B_2 reaction is the strong successor complex $\text{Zn}(\text{acac})_2 \cdot \text{Cu}(\text{PS})_2$.

It is worth recalling 1) that $\text{Zn}(\text{NS})_2$ also is a very weak complex compared To $\text{Ni}(\text{NS})_2$ and $\text{Cu}(\text{NS})_2$ [9] and 2) that it reacts with polynuclear target $(\mu_4\text{-O})\text{N}_4\text{Cu}(\text{Ni}(\text{H}_2\text{O}))_3\text{Cl}_6$ via precursors with moderate and measurable equilibrium constants B_1 . By contrast, the reaction of the same target $(\mu_4\text{-O})\text{N}_4\text{Cu}(\text{Ni}(\text{H}_2\text{O}))_3\text{Cl}_6$ with $\text{Ni}(\text{NS})_2$ is

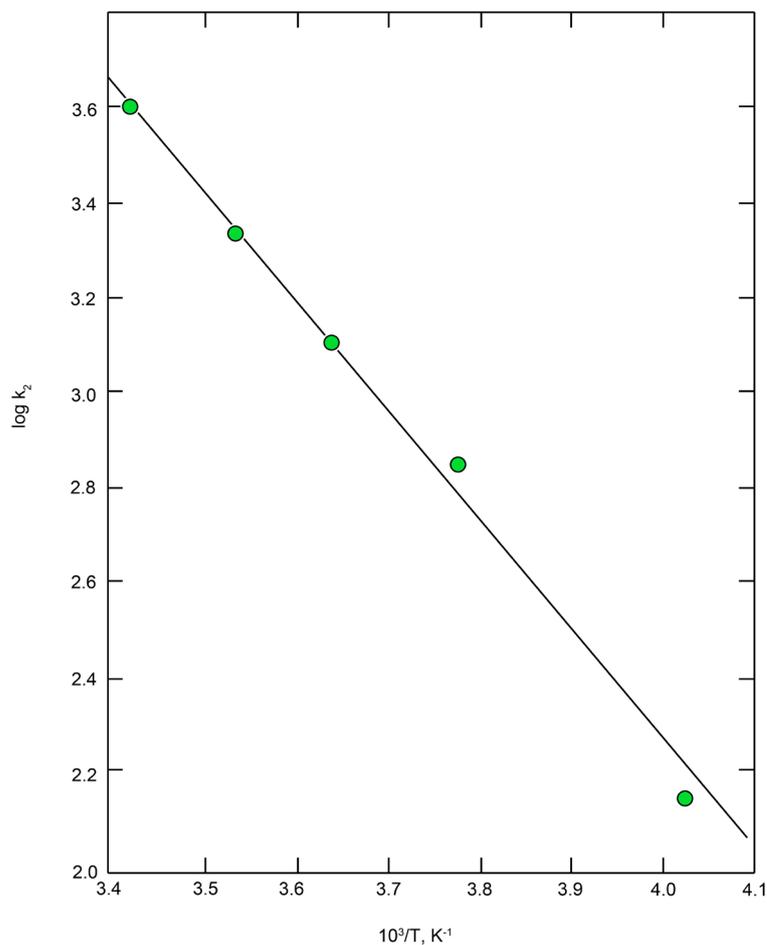


Figure 3. Plot of $\log k_2$ vs $1/T$ for the reaction of A with $Zn(PS)_2 B_2$ in methylene chloride.

third-order and must therefore involve very weak precursors [20].

An ability of zinc transmetalators to ring-open to form more stable precursors than nickel reagents would lead us to expect either the same kind of behavior as in the reaction of A with B_2 or a situation where the precursor was so stable that the reaction rate is independent of $[A]$ [22] [23]. However, the second-order rate law for the reaction of A with zinc reactant B_2 leads us strongly to suspect that the slow step is precursor formation followed by very rapid, irreversible metal exchange.

Figure 6 of Ref. [21] shows activation parameter correlations for second-order transmetalations of polynuclear copper(II) targets with reactants C and the corresponding S-methylbenzylidenehydrazinecarbodithioate transmetalators D. The latter are generally more thermodynamically stable than C with the same M [10]. The lowest line in that figure M [21] correlates six kinetic data pairs, four of which are for reactants of D ($M = Zn$) with targets $(\mu_4-O)N_4CuX_6$ ($X = Cl$ or Br) in methylene chloride or nitrobenzene. The data pair ($\Delta H_2^\ddagger = 10.7$ kcalmol $^{-1}$, $\Delta S_2^\ddagger = 5$ cal deg $^{-1}$ mol $^{-1}$) for the reaction of A with $Zn(PS)_2 (B_2)$ fits this lower line. This suggests that the seven correlated data sets refer to rate-determining precursor formation in these transmetalation systems. All are irreversible and the key to this assignment is the apparent slow step in the A/B_2 system.

4. Conclusion

$M(PS)_2$ complexes B is less thermodynamically stable than the corresponding $M(NS)_2$ complexes C. On this basis we might expect them to be faster transmetalators than reagents $M(NS)_2$ (M common in B or C) for a given target. Indeed, $Zn(PS)_2 (B_2)$ seems to transmetalate A via rate-determining precursor formation. However, my work shows that $Ni(PS)_2 (B_1)$ is a stronger precursor former than C_1 with A and that this results in lower metal

exchange rates. Nevertheless, $M(PS)_2$ transmetalation systems might have even greater specificity than that having been found with S-methyl isopropylidenehydrazinecarbodithioate ligands [9] [20] [21] [29]. This possibility and the reactions of dithiophosphate transmetalators with other monomeric and polynuclear targets should be explored in the future work.

Acknowledgements

I would like to thank Chemistry Department Faculty of Science, Alexandria University, for support and Professor Mohamed A. El-Sayed for valuable discussions and comments.

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