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An Observation of Compensation Effects between Enthalpy and Entropy Changes in the Interaction of Nickel-2,2′-bipyridine Complexes with Olefins

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Synopsis. Compensation effects in the thermodynamic parameters ΔH° and ΔS° in the coordination of olefins with Ni(bpy) and $\mathrm{NiR_2(bpy)}$ (bpy=2,2′-bipyridine) and in the kinetic parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in reactions of $\mathrm{NiR_2(bpy)}$ with olefins have been observed; factors governing these compensation effects are discussed.

Coordination of an olefin to a transition metal having a σ-metal–carbon bond with a resultant activation of the metal–carbon bond constitutes a key step in various transition-metal promoted reactions of olefins. Despite the tremendous increase in the number of isolated olefin-metal complexes,[1] thermodynamic and kinetic data concerning the interaction of olefins with transition-metal complexes are quite meager and this situation seems to hinder the further understanding of the nature of the olefin-metal interaction. Dialkyl(2,2′-bipyridine)nickel(II), $\mathrm{NiR_2(bpy)}$ **1** (bpy=2,2′-bipyridine, R=$\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_3H_7}$, i-$\mathrm{C_4H_9}$), and olefin-coordinated zerovalent nickel complexes, Ni(olefin)n(bpy) **2** (n=1 or 2), have proved to be quite amenable to a quantitative investigation of the olefin-metal interaction.[2,3] Previous studies have established that the interaction of **1** with an olefin proceeds through the following reaction steps:

$$\underset{\mathbf{1}}{\mathrm{NiR_2(bpy)}} + \text{olefin} \overset{K_1}{\rightleftarrows} \underset{\mathbf{2}}{\mathrm{NiR_2(bpy)(olefin)}} \qquad (1)$$

$$\underset{\mathbf{2}}{\mathrm{NiR_2(bpy)(olefin)}} \xrightarrow{k} \underset{\mathbf{3}}{\mathrm{Ni(bpy)(olefin)}} + 2\mathrm{R} \qquad (2)$$

$2\mathrm{R}=\mathrm{C_2H_6}$, $\mathrm{C_4H_{10}}$ for $\mathrm{R}=\mathrm{CH_3}$, $\mathrm{C_2H_5}$

$2\mathrm{R}=\mathrm{C_3H_6}+\mathrm{C_3H_8}$, $\mathrm{C_4H_8}+\mathrm{C_4H_{10}}$ for $\mathrm{R}=\mathrm{C_3H_7}$, $\mathrm{C_4H_9}$

Furthermore, the stability constants of the zerovalent olefin-nickel complexes in the following equilibria have been evaluated:

$$\mathrm{Ni(bpy)(solvent)} + \text{olefin} \overset{K_3}{\rightleftarrows} \underset{\mathbf{3}}{\mathrm{Ni(bpy)(olefin)}} + \text{solvent} \qquad (3)$$

Examination of the enthalpy change (ΔH°) and entropy change (ΔS°) in equilibria (1) and (3) and of Eyring's enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) in the splitting of Ni–C bonds in **1** has revealed the presence of clear compensation effects between ΔH° and ΔS°, as well as between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Here, results are reported in order to provide the basis for further discussions on transition metal-olefin interactions.

Compensation Effects between ΔH° *and* ΔS° *in the Coordination of Olefins with Ni(bpy) and* $\mathit{NiR_2(bpy)}$. Figure 1 clearly demonstrates the presence of compensation effects in equilibria (1) and (3). Plots of ΔH° and ΔS° values for reaction (3) give a straight line over a very wide range (line A in Fig. 1), except for maleic anhydride, the only α,β-disubstituted olefin among the olefins examined. The plot of ΔH° and ΔS° values for Eq. 1 also gives a straight line with a steeper slope (line B in Fig. 1).[4] For the sake of numerical comparison, the following expression is used

$$\Delta S^\circ = C_1 \Delta H^\circ + C_2, \qquad (4)$$

where C_1 and C_2 are constants derived from the slopes and intercepts of straight lines A and B in Fig. 1. These values are tabulated in Table 1.

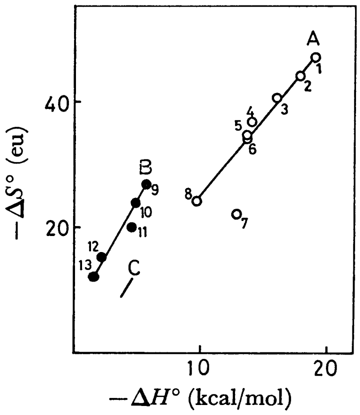

Fig. 1. The plots of ΔS° against ΔH° in the equilibria (1) and (3). Ni(bpy), line A: (1) acrylaldehyde, (2) acrylamide, (3) acrylonitrile, (4) methacrylonitrile, (5) methyl acrylate, (6) methyl vinyl ketone, (7) maleic anhydride, (8) methyl methacrylate. For $\mathrm{NiR_2(bpy)}$, line B: (9) R=$\mathrm{C_2H_5}$, acrylaldehyde, (10) R=n-$\mathrm{C_3H_7}$, acrylonitrile, (11) R=$\mathrm{C_2H_5}$, acrylonitrile, (12) R=$\mathrm{CH_3}$, acrylonitrile, (13) R=i-$\mathrm{C_4H_9}$, acrylonitrile. The straight line C was taken from Fueno's paper.[5]

TABLE 1. THE COMPENSATION EFFECT BETWEEN ΔH° AND ΔS° IN THE COORDINATION OF OLEFINS WITH METALS

Metal	Olefin	$C_1 \times 10^3$ (eu/(cal/mol))	C_1T (at T=300)	C_2 (eu)
Ni(bpy)	β-Unsubstituted vinyl compound	2.1	0.6	+1
$\mathrm{NiR_2(bpy)}$	β-Unsubstituted vinyl compound	3.3	1.0	+6
$\mathrm{Ag^+}$	β-Unsubstituted vinyl ether[a]	3.0	0.9	−2

a) The values for the argentation of β-unsubstituted vinyl ethers were taken from Ref. 5.

Fueno and coworkers have previously observed a similar compensation effect in the argentation of vinyl ethers and alkenes over a narrower range as shown by line C in Fig. 1.⁵⁾ The C_1 and C_2 values are also included in Table 1. It is noteworthy to observe the presence of a compensation effect over such a wide range in the coordination of olefins bearing a variety of electron-withdrawing substituents with the nickel complexes, as well as in the argentation of olefins bearing electron-releasing substituents. Although it may be fortuitous, it is intriguing to observe that the extension of line A in Fig. 1 passes through line C. The presence of a compensation effect over this wide range implies that the interaction between the nickel complex and the variety of olefins is dominated by a single factor, namely, the complexation of the olefins with nickel through an olefinic double bond. The side-on coordination of methyl acrylate through the double bond to nickel in the solid Ni(bpy)(methyl acrylate)$_2$ has been recently established.⁶⁾ The lesser gradient in line A with a C_1T value of 0.6 at 300 K with respect to line B implies the greater contribution of the enthalpy effect on the stability of the π-olefin complexes **3**. This is in line with the anti-parallel relationship observed between log K_2 and the energy level of the π^*-orbital of the olefins,²⁾ a fact indicating the importance of back-donation from nickel to the olefin, which determines the stability of **3**.

In Eq. 1, on the other hand, the value of C_1T at room temperature is very close to unity, indicating the complete cancellation of the enthalpy change by the entropy change. In this case, the contribution of entropy is considered to be more important for the stabilization of the π-complexes **2** than in reaction (3) and the freedom of internal rotation of the nickel-bonded alkyl groups may exert a significant effect on the stability of **2** as reflected by the considerably smaller values of $\Delta S°$ and $\Delta H°$ observed in the complexation of acrylonitrile with the bulky isobutylnickel complex than those obtained for the propylnickel complex.

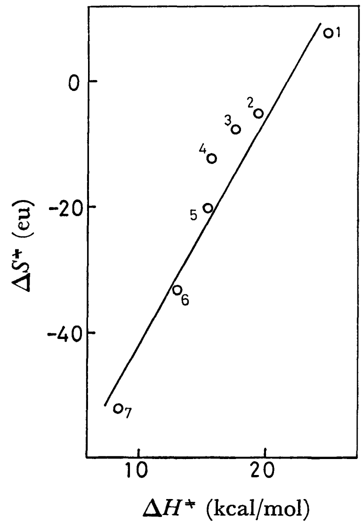

Fig. 2. Relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in the reaction of Ni(C_2H_5)$_2$(bpy) with olefins. (1) methacrylonitrile, (2) acrylamide, (3) methyl vinyl ketone, (4) acrylaldehyde, (5) methyl acrylate, (6) styrene, (7) methyl methacrylate.

These results suggest that a seemingly small variation in the stability constant of a π-complex may not reflect a greater intrinsic change of interaction between an olefin and a transition-metal complex because of the presence of the compensation effect.

Compensation Effect between the Enthalpy of Activation and Entropy of Activation for the Splitting of Nickel–alkyl Bonds Induced by Olefin Coordination. Figure 2 shows that there is a fairly good correlation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for reactions (1) and (2), which were taken from a previous paper.²⁾ The slope of the line in Fig. 2 is about 1/300 deg^{-1} which corresponds to a value of 1.0 for $T\Delta S^{\neq}/\Delta H^{\neq}$ at room temperature, indicating an almost complete cancellation of the entropy and enthalpy effects. The breaking of the Ni–C bond by the interaction with an olefin is a second-order reaction, whose rate constant can be expressed by K_1k in reactions (1) and (2). Since it is observed that $T\Delta S° \fallingdotseq \Delta H°$ in Eq. 1, the present compensation effect for the reaction allows us to deduce that there is a similar compensation effect for the splitting of Ni–alkyl bonds in the olefin coordinated diethyl (2,2′-bipyridine)nickel complex **2** given by reaction (2), namely, the acquired activation enthalpy is almost completely cancelled at room temperature by an increase in the entropy in the activated complex to be thermolyzed. A similar compensation effect in the thermolysis of alkylcopper complexes having tertiary phosphine ligands⁷⁾ has been observed.

References

1) For example, M. Herberhold, "Metal π-Complexes," Elsevier Publishing Co., Amsterdam, London, New York (1972) and references cited therein.

2) (a) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971); (b) *ibid.*, **93**, 3360 (1971).

3) T. Yamamoto, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 191 (1976).

4) The data for line B in Fig. 1 are taken from previously published data obtained by a visual method for the coordination of acrylaldehyde and acrylonitrile with a series of NiR$_2$(bpy).²⁾ Later, somewhat more accurate data for the ethylnickel complex were obtained by an NMR method.³⁾ The values of $\Delta H°$ and $\Delta S°$ obtained by the NMR method also fall along the same straight line B although they have values that are somewhat more negative than those obtained by the visual method.

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7) A. Miyashita, Ph. D. Thesis, Tokyo Institute of Technology (1975).