

## Transition-Metal Complex Formation with Phenyl Isocyanate

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### Synopsis

Complex formation between phenyl isocyanate and cobalt or manganese naphthenate in benzene was determined by the mole ratio method. Complexes of 3:1 for cobalt and 2:1 for manganese were found. The method of analysis in this study utilized the characteristic transition-metal visible absorption spectra. Effects of time and metal-salt solution stability are noted.

### Introduction

Several investigations have been made to determine the effects of metals in the catalysis of isocyanate-alcohol reactions. Britain and Gemeinhardt<sup>1</sup> suggested that the metal salt activated the reagents by complexation and postulated a mechanism of the catalysis. Robins<sup>2</sup> screened a large number of metal compounds in a variety of isocyanate-alcohol systems and found that the catalytic activity is enhanced by the presence of certain groups  $\alpha$ ,  $\beta$ , or even  $\gamma$  to the carbon carrying the reactive —OH group. Smith<sup>3</sup> observed small shifts in the infrared spectra of toluene solutions of isocyanates or polyols when stannous salt catalysts were added. He observed the same spectral shifts for isocyanate-alcohol catalyst mixtures and therefore concluded that metal catalysts enhance urethane formation by activation of both reactants by means of a ternary complex. Frisch et al.<sup>4</sup> examined the infrared spectra of 10–20% dibutyltin dilaurate or stannous 2-ethylhexoate in 1-methoxy-2-propanol or phenyl isocyanate and were unable to observe any band shifts or intensity changes resulting from complex formation. These investigators also examined the phenyl isocyanate-dibutyltin dilaurate system by NMR spectroscopy and phenyl isocyanate-lead naphthenate or stannous octoate systems by ultraviolet spectroscopy and found no evidence of isocyanate-catalyst complexes in either case.

A search of the literature reveals that there is no unambiguous quantitative proof of the existence of metal complexes in these systems. The purpose of our study was to determine whether complexes are formed with metal catalysts and phenyl isocyanate and, if so, to characterize the complex species in terms of their stoichiometries.

### Experimental

Woo and Liu<sup>5</sup> measured the absorption spectra of several isocyanates in the gas phase and found that each exhibited characteristic bands in the ultraviolet. Initially, therefore, we attempted to detect complex formation by characterizing the ultraviolet absorption spectra of the isocyanate group in solvents whose limiting wavelengths are less than 220  $m\mu$ , which would thereby permit the study of changes in these spectra when complexing agents were added. All materials used in this phase of the study were reagent-grade, and solvents were distilled from suitable drying agents prior to use. The solubility of silver isocyanate was measured in several anhydrous solvents by placing a weighed amount of the salt in a flask filled with solvent and shaking for 2 hr. The solvents employed were methanol, isopropanol, diethyl ether, *n*-heptane, cyclohexane, and isooctane. In each case it was found that the solubility of silver cyanate was less than  $5 \times 10^{-5}$  mole/liter. This limited solubility unfortunately precluded the characterization of isocyanate spectra in these solvents.

A second approach with metal catalysts (donated by the Harshaw Chemical Co.) and reagent-grade benzene (distilled from sodium wire) proved to be more successful. A typical run consisted of weighing the catalyst and adding freshly distilled benzene to give the desired concentration. Stock solutions of phenyl isocyanate in benzene were prepared from a freshly opened bottle of reagent-grade phenyl isocyanate (Eastman Kodak). The phenyl isocyanate was then diluted to a concentration equal to the catalyst concentration. The spectra of all solutions were determined at room temperature in suitable quartz cells with a Cary Model 14 spectrophotometer. Phenyl isocyanate has no visible absorption spectrum, but the transition-metal catalyst spectra could be characterized in terms of maxima, minima, and molar absorptivities, and they were found to obey the Beer-Lambert law over the concentration range considered. A series of solutions were prepared by mixing stock solutions of phenyl isocyanate and metal catalysts, to give a range of concentrations. The range of  $[\text{C}_6\text{H}_5\text{—NCO}]/[\text{catalyst}]$  ratios used in this study was 1:1 to 7:1. The spectra of each of these solutions was recorded continuously, and the cobalt was found to undergo no further change after 30 min., whereas the manganese became stable after 5 min. Therefore, all data were collected in accordance with these times and treated by the mole ratio method,<sup>6</sup> to determine the extent of complex formation. This method consists of choosing a wavelength corresponding to a maximum of the spectrum of the pure catalyst and plotting the absorbance  $A$  of various mixtures against the mole ratio ( $[\text{C}_6\text{H}_5\text{—NCO}]/[\text{catalyst}]$ ). These curves consisted of two linear portions that intersected at the mole ratio corresponding to the coordination number of the metal.

The possible effect of atmospheric humidity in this procedure was checked by taking rigorous precautions in some runs to eliminate moisture. These included treating all glassware with methylchlorosilane vapors according to Hawkins and Wilson,<sup>7</sup> distilling the solvent from freshly pressed sodium

wire and allowing it to pass through an alumina column, redrying benzene solutions of catalyst by azeotropic distillation, and finally carrying out all subsequent sample preparation in a dry box under a dry nitrogen atmosphere. Glass-stoppered absorption cells were also filled in the dry box. The complete agreement of results obtained with and without these precautions indicated that our measurements were not noticeably affected by atmospheric moisture.

### Discussion

A number of investigators have studied isocyanate-alcohol reactions over a range of experimental conditions. Some of the solvents studied include dioxane,<sup>2</sup> toluene,<sup>3</sup> chloroform,<sup>9</sup> and benzene.<sup>10</sup> Robins<sup>2</sup> screened a large number of metal naphthenates ( $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Hg}^{2+}$ , and  $\text{Bi}^{3+}$ ), octoates ( $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Sn}^{2+}$ ), and dibutyltin dilaurate catalysts. We first attempted to devise a spectrophotometric method of studying complex formation that would be applicable to a wide variety of metal catalysts. The method would have consisted of characterizing the ultraviolet absorption spectrum of the isocyanate group in suitable solvents and then measuring changes in its spectrum as metal catalysts were added. As the investigation progressed, we encountered difficulty in dissolving solid isocyanate salts in benzene. Then, when we investigated the ultraviolet spectra of phenyl isocyanate, we found that the solvent absorption bands overlapped the region of interest, which necessitated abandoning this method.

A second approach for studying isocyanate-catalyst complex formation based on the visible absorption spectra of the metal catalysts proved to be successful. The most significant distinguishing characteristic of the transition-metal ions is that they possess unfilled *d* orbitals. The visible spectral activity of these ions involves transitions of the metal *d* electrons among several split energy levels established by the strength and symmetry of a particular ligand field. Obviously, these factors limit the application of this technique to the transition-metal catalysts. In this work the catalysts chosen, namely cobalt and manganese naphthenates, were those whose efficiency have been demonstrated in isocyanate-alcohol reactions.

Benzene solutions of cobalt naphthenate exhibit absorption maxima at 578 and 525  $\text{m}\mu$  and minima at 540 and 425  $\text{m}\mu$ . Below 425  $\text{m}\mu$  there is a large increase in absorption (bands unresolved), probably due to charge-transfer transitions. The long-wavelength transition at 578  $\text{m}\mu$  (molar absorptivity  $\approx 59$ ) exhibits a maximum change when phenyl isocyanate is added, so the majority of our data for the cobalt system was obtained at this wavelength. Corresponding solutions of manganese exhibit continuously increasing absorption between 625 and 425  $\text{m}\mu$ , where intense charge-transfer absorption begins. This spectrum has no true maximum, so absorption at 475  $\text{m}\mu$  (molar absorptivity  $\approx 2.1$ ) was used for obtaining data for this system. The absorption curve at this wavelength is undergoing a minimum change of slope over the wavelength range considered. The

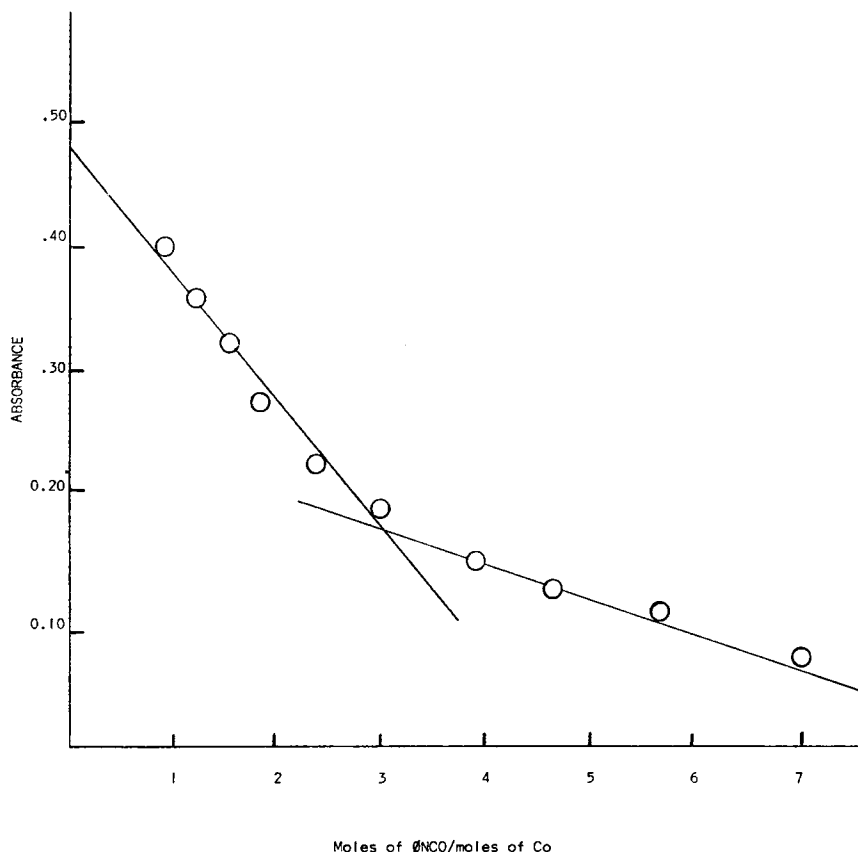


Fig. 1. Mole ratio plot of cobalt-phenyl isocyanate complex at 578  $\text{m}\mu$ .

small molar absorbancy is indicative of the  $\text{Mn}^{2+}$  species, which has five  $d$  electrons, and Orgel energy-level diagrams<sup>11</sup> indicate that all  $d-d$  transitions in an octahedral or tetrahedral field of symmetry are forbidden.

It was necessary to prepare fresh benzene solutions of metal catalysts for each run. Furthermore, in the case of manganese it was necessary to use a sample of catalyst that had not previously been exposed to air. It was observed that the spectral characteristics of stock solutions changed gradually from day to day, even when stored in air-tight glass-stoppered containers. Catalysis by light is not solely responsible for these changes, since similar results were obtained with solutions stored in darkness.

For the determination of the mole ratio of phenyl isocyanate to metal catalyst in the complex the concentration of the catalyst was held constant (Co,  $1.37 \times 10^{-2}$  mole/liter; Mn, 0.164 mole/liter) and the ratio of phenyl isocyanate to catalyst varied from 1:1 to 7:1. Absorbances measured at 578  $\text{m}\mu$  for cobalt and 475  $\text{m}\mu$  for manganese are plotted against the mole ratios, as shown in Figures 1 and 2. A sharp break in the lines is observed at the mole ratio corresponding to the stoichiometry of the complex. Analysis

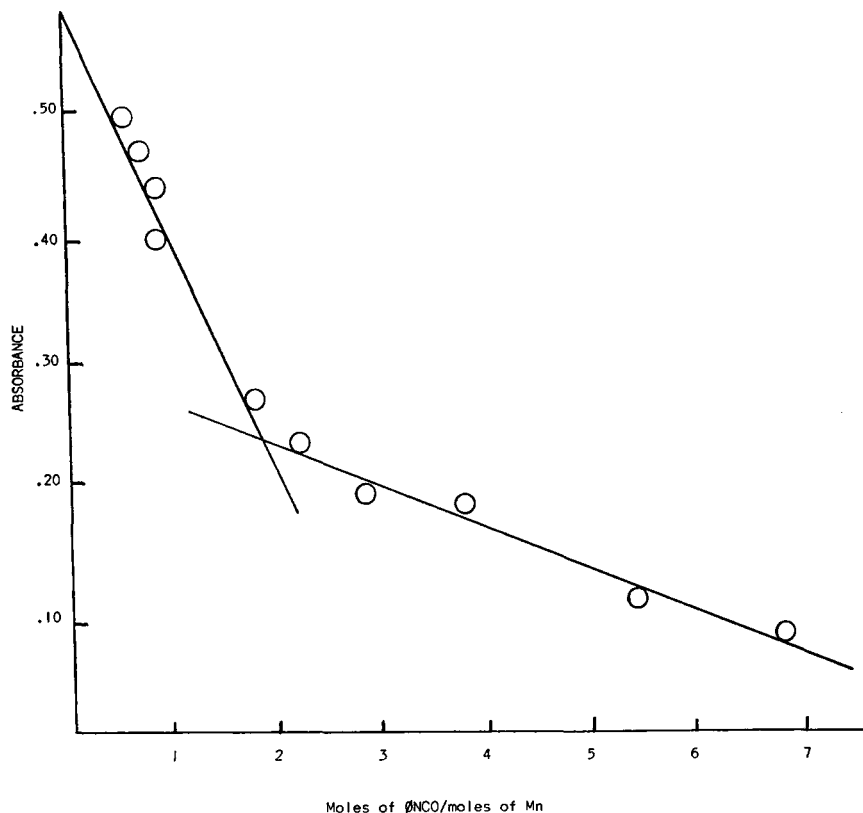


Fig. 2. Mole ratio plot of manganese-phenyl isocyanate complex at 475  $\mu$ .

of the data obtained for a series of runs indicates that the mole ratio of phenyl isocyanate to metal catalyst is  $3.0 \pm 0.1$  for cobalt and  $2.0 \pm 0.1$  for manganese. It is to be noted that the slope of the line past the break is not zero, although a zero slope would be predicted if one assumed that no additional phenyl isocyanate were complexed beyond this point. However, this behavior is not unusual, since Gerlach and Frazier,<sup>12</sup> in using the mole ratio method to study the complex formed by  $\text{Hg}^{2+}$  and diphenylcarbazone, observed a nonzero slope past the break in the curve. Their results were subsequently verified when identical results were obtained with a continuous-variation method. The nonzero slope may be interpreted as meaning that the complexes are dissociated to some extent in the solution.

*sym*-Diphenylurea identified by its infrared spectrum is formed in small amounts when the more concentrated solutions of metal catalyst and phenyl isocyanate are allowed to stand for long periods after mixing. The urea formed even after rigorous steps were taken to remove and exclude moisture (see experimental) appears to be the result of reaction of water with the isocyanate. It is likely that metal-coordinated water, which would not be removed by the drying methods used, is responsible.

Smith<sup>3</sup> observed small shifts in the infrared spectra of isocyanate–alcohol–2-ethylhexoate solutions and concluded that ternary complexes are formed. Frisch et al.<sup>4</sup> used NMR evidence to show that 1-methoxypropanol–metal–catalyst complexes are formed with dibutyltin dilaurate and lead naphthenate, although they were unable either to observe infrared shifts in phenyl isocyanate–dibutyltin dilaurate solutions or to find evidence of complex formation in the ultraviolet spectra of phenyl isocyanate–stannous octoate or lead naphthenate in cyclohexane solution. Unfortunately, post-transition metals exhibit no visible absorption spectra; therefore, none of these previous studies can be checked by our method, which depends on changes in the visible absorption spectrum of the central metal atom. One might infer from this study and from previous investigations that a common catalytic mechanism is not operative in transition and post-transition metals.

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