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NOTE

Solvent effects on the kinetics of substitution reactions of nickel carbonyl

The kinetics and mechanism of the reaction of $Ni(CO)_4$ with phosphines and phosphites, L, to form $Ni(CO)_3L$ have been studied rather extensively[1,2]. It is generally agreed that the reaction proceeds according to a rate law which exhibits a first order dependence on the concentration of $Ni(CO)_4$ but is independent of the concentration and nature of the phosphine or phosphite. A simple dissociative, S_N1, mechanism was postulated for the reaction[1].

$$Ni(CO)_4 \xrightarrow[\text{slow}]{-CO} Ni(CO)_3 \xrightarrow[\text{fast}]{+L} Ni(CO)_3L$$

The activated complex involved in the rate-determining step presumably contains only three strongly coordinated CO groups plus the dissociating CO. The relatively low coordination number of the nickel in the transition state could allow it to interact with the solvent rather strongly making the rates of these reactions strongly dependent upon the nature of the solvent. Previous work by Heck[1] showed a slight difference for the reaction of $Ni(CO)_4$ with $P(C_6H_5)_3$ in ethyl ether (2.8×10^{-4} sec^{-1}) and in toluene (4.3×10^{-4} sec^{-1}) at 0.0°. On the other hand, activation parameters for this reaction were, within experimental error, identical in heptane, acetonitrile and toluene[2]. The present paper considers a large number of solvents, and activation parameters are found not to be the same in all solvents.

Experimental

Nickel carbonyl was distilled under vacuum before use. The bicyclic phosphite, $P(OCH_2)_3CCH_3$, was prepared according to the literature[3] and $P(C_6H_5)_3$ was used as obtained from Matheson, Coleman, and Bell Co. The following solvents were reagent grade and were not purified further: nitromethane, heptane, chloroform, ethyl ether, cyclohexanone, ethylacetate, methylbenzoate, triethylamine, acetonitrile, acetone, *o*-xylene, benzene, toluene, and nitrobenzene. Cyclohexane, anisole, 1,2-dichloroethane, chlorobenzene, cyclohexene, and mesitylene were distilled under a nitrogen atmosphere. sym-Tetrachloroethane was shaken with concd. H_2SO_4 and distilled from P_4O_{10} in an N_2 atmosphere. Tetrahydrofuran was first dried over KOH, then over $LiAlH_4$ and finally distilled under N_2. Dioxane was distilled from sodium under an N_2 atmosphere.

The kinetic studies were carried out by thermostatting, separately, solutions of $Ni(CO)_4$ and ligand in a constant temperature bath. After 15–30 minutes the solutions were mixed and introduced into the thermostatted infrared cell. This cell consisted of aluminum front and back plates which were drilled to allow thermostatted water to be circulated through them. Between these plates were placed the NaCl plates which were separated by a lead spacer. The temperature of the reaction solution was determined by a small thermistor which was placed into a hole drilled into the edge of one of the NaCl plates. It was not inserted so far that it was in the light path but as closely to that point as possible. Petroleum jelly surrounded the thermistor to improve contact with the NaCl plate. The temperature of the cell as measured by the thermistor was the same as that of the circulating water at 25.0° but was slightly higher than the constant temperature water at 16.5°. The temperature of the reaction was taken as that measured by the thermistor. The infrared cell was inserted into a Beckman IR-8 infrared spectrophotometer and the wavelength was set at the intense absorption (2050 cm^{-1}) of $Ni(CO)_4$. Using an auxiliary recorder, a continuous record of the disappearance of $Ni(CO)_4$ was plotted. These data were re-plotted according to a first-order rate law, *i.e.* ln $(A-A_\infty)$ *versus* time, where A and A_∞ are the absorbances at any given time and at the end of the reaction, respectively. The first order rate constants, k, were reproducible to within at least 3% If the C–O stretching region was continuously scanned, it was noted that the disappearance of the $Ni(CO)_4$ absorption was accompanied by the growth of product, $Ni(CO)_3P(C_6H_5)_3$, peaks at 2065 and 1990 cm^{-1}, as expected[4]. The initial concentration of $Ni(CO)_4$ in these reactions was 2.5×10^{-3} M while ligand concentrations varied from 2.5×10^{-2} to 0.25 M. Activation parameters and their standard deviations were calculated with a least squares computer program[5].

All solvents, except anisole and mesitylene, gave colorless solutions of $Ni(CO)_4$. These two solvents yielded yellow solutions, but the C–O stretching frequency of $Ni(CO)_4$ was virtually the same in these as in all other solvents. The color suggests the formation of a charge-transfer complex between $Ni(CO)_4$ and the aromatic molecules.

Results and discussion

The reaction of $Ni(CO)_4$ with $P(C_6H_5)_3$ and $P(OCH_2)_3CCH_3$ proceeds according to a rate law which is independent of the phosphine concentration but is first order in $Ni(CO)_4$. This behavior was observed in all solvents studied. The first order rate constants given in Table 1 are averages of at least two but usually 5 different rate determinations. The differences in rate are small, but there are strong indications of solvent participation in the reaction. There is no suggestion that the dielectric constant of the solvent is a significant factor in determining the rates.

TABLE 1

RATES OF THE REACTION $Ni(CO)_4 + P(C_6H_5)_3 \rightarrow Ni(CO)_3P(C_6H_5)_3 + CO$ IN VARIOUS SOLVENTS AT 25.0°

Solvent	$10^3\ k(sec^{-1})$	*Solvent*	$10^3\ k(sec^{-1})$
sym-Tetrachloroethane	3.50	Chlorobenzene	13.4
Cyclohexane	6.87	Cyclohexene	13.7
Nitromethane	7.32	Tetrahydrofuran	13.8
Heptane	8.54	Triethylamine	14.1
Nitrobenzene	9.04	Acetonitrile	14.1
Chloroform	9.65	Acetone	14.2
Ethyl ether	9.78	Dioxane	14.6
Anisole	10.8	*o*-Xylene	15.8
1,2-Dichloroethane	11.5	Mesitylene	17.4
Cyclohexanone	11.7	Benzene	18.9
Ethyl acetate	12.0	Toluene	19.4
Methyl benzoate	12.6		

On the other hand, solvents which contain such traditional donor atoms as N and O tend to accelerate the rates beyond the non-coordinating solvents. Representative solvents which interact through a donor atom are acetonitrile, tetrahydrofuran and triethylamine, all of which are known to form complexes of varying stabilities with transition metals. Even more effective than the one atom donor solvents are those which are derivatives of benzene. With the exception of anisole, it is the benzene derivatives which contain electron-releasing groups that yield the fastest rates. Deactivated rings as in chloro- or nitrobenzene do not effectively accelerate the rate of reaction. The relative abilities of the various aromatic solvents to alter the rate of reaction parallels the stabilities of well-known complexes of substituted benzenes with chromium and molybdenum. Benzenes substituted with electron-releasing groups form more stable complexes than those with electron-withdrawing groups[6,7]. That the solvent cyclohexene noticeably enhances the rate of reaction over that in cyclohexane suggest that there is some interaction between the olefinic π-system and the nickel atom. In general, the rates of reaction correlate with the C–O stretching frequency[8] of $Ni(CO)_4$ in various solvents. The rate of reaction increases as the C–O frequency of $Ni(CO)_4$ decreases. A low C–O frequency presumably indicates strong solvent/$Ni(CO)_4$ interactions.

The rates of reaction with $P(C_6H_5)_3$ in cyclohexane and in toluene were measured at other temperatures. In cyclohexane at 16.5, 19.0, 20.5, and 23.5°, the first order rate constants were 1.77, 2.77, 3.27, and 5.35×10^{-3} sec^{-1}. In toluene at 19.0 and 23.5°, the rate constants were 9.40 and 15.8×10^{-3} sec^{-1}. Activation parameters for the reaction of $Ni(CO)_4$ with $P(C_6H_5)_3$ in these two solvents follow:

Cyclohexane	ΔH^* 26.6±0.7 kcal/mole	ΔS^* 20.9±2.3 e.u.
Toluene	ΔH^* 20.4±0.6 kcal/mole	ΔS^* 2.0±1.9 e.u.

The limits of error are given as one standard deviation. Clearly the enthalpy of activation is lower in toluene than in cyclohexane, but the entropy is also substantially lower. This result suggests an interaction of toluene with $Ni(CO)_4$ in the transition state to assist in the dissociation of a CO group, but this interaction restricts the freedom of the toluene molecules thus lowering the entropy of activation. Although the lowering of ΔH^* accelerates the rate of reaction, the lowering of ΔS^* slows the reaction. The net effect is that the observed rate does not change very much from cyclohexane to toluene.

Since other workers had reported values for ΔH^* and ΔS^* of 21 ± 1 kcal/mole and 2±2 e.u., respectively, in both heptane and toluene, it was desirable to check our activation parameters in a reaction with another phosphorus donor. The reaction of $Ni(CO)_4$ with $P(OCH_2)_3CCH_3$ at 16.5, 20.5, and 25.0° in toluene gave first order rate constants of 5.95, 9.77, and 18.0×10^{-3} sec^{-1}, respectively. The values for ΔH^* and ΔS^* were 22.0±0.4 kcal/mole and 7.2±1.2 e.u., respectively. Within two standard deviations these values are the same as those for the reaction with $P(C_6H_5)_3$ in toluene. Thus the enthalpy of activation for substitution reactions of $Ni(CO)_4$ is approximately 5 kcal/mole lower in toluene than in cyclohexane solvent.

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