Studies on Solid–Solid Reactions between 4-Methylbenzenamine and $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$

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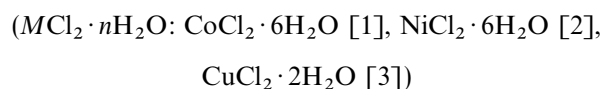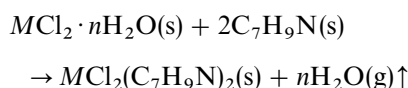
Dichlorobis(4-methylbenzenamine) cobalt(II), nickel(II), and copper(II) were synthesized individually via direct solid–solid reactions between 4-methylbenzenamine and $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$ at 20°C and were characterized by spectral studies. Interesting phenomena of the color change and evidently different formation rates of these reactions were observed when performed at 0°C. Furthermore, the concept of "inert" and "labile" complexes is applied for the first time to explain the rates of the substitution reactions in the solid state.

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INTRODUCTION

Here is our report on a new technique (1) for the preparations of the complexes of 4-methylbenzenamine with Cu(II), Co(II), and Ni(II) through the following reactions in the solid state at room temperature (20°C):

$$MCl_2 \cdot nH_2O(s) + 2C_7H_9N(s)$$

$$\rightarrow MCl_2(C_7H_9N)_2(s) + nH_2O(g)\uparrow$$

$$(MCl_2 \cdot nH_2O: \; CoCl_2 \cdot 6H_2O \; [1], \; NiCl_2 \cdot 6H_2O \; [2],$$

$$CuCl_2 \cdot 2H_2O \; [3])$$

Based on the observations of the reactions taking place at 0°C and the distinctions of the system, we proposed a rate controling step of these substitution reactions and tried to shed light on the kinetics of this particular system in respect of electron configuration (2).

EXPERIMENTAL

1. Apparatus

XRD patterns were recorded on a Rigagu D/Max-RA model X-ray diffractometer with Cu target and graphite monochromator. Far-infrared spectra were measured on a Bruker IFS 66V FTIR. Ultraviolet and visible spectra were obtained from a Shimadzu UV-240 spectrophotometer.

2. Reagents

$CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and 4-methylbenzenamine were analytical reagents. They were used after being ground and passed through a 100-mesh sieve.

3. Preparations and Reactions

Preparations. The solid reactants $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and 4-methylbenzenamine were mixed individually at 1:2 stoichiometric ratio at room temperature (20°C). As soon as the reactants were mixed, there were fast color changes in reactions [1] and [3]: one from purplish red to sky blue and the other from blue to brown. After being ground for 5 min, all the reactants in the two reactions were exhausted and new peaks appeared in comparison with the XRD patterns of the products obtained in solution (3,4). In contrast, the color of the mixture in reaction [2] did not start changing from green to pale yellow until after having been ground for about 5 min. After 15 min, the XRD pattern of the solid product in reaction [2] was identical to that of the product in solution (5) (Fig. 1).

In addition, the ultraviolet and visible spectra and far-infrared spectra of the three products confirmed previous results (3, 6).

After the products were washed with acetone, the productive rates were respectively 93, 95, and 96%.

Reactions. When the reactions were performed at 0°C, more obvious phenomena were observed. Although the rates for reactions [1] and [3] hardly changed as compared with those at 20°C which were very fast, no color change in reaction [2] could be noticed even after the mixture had been ground for 10 min and allowed to stand for 2 h.
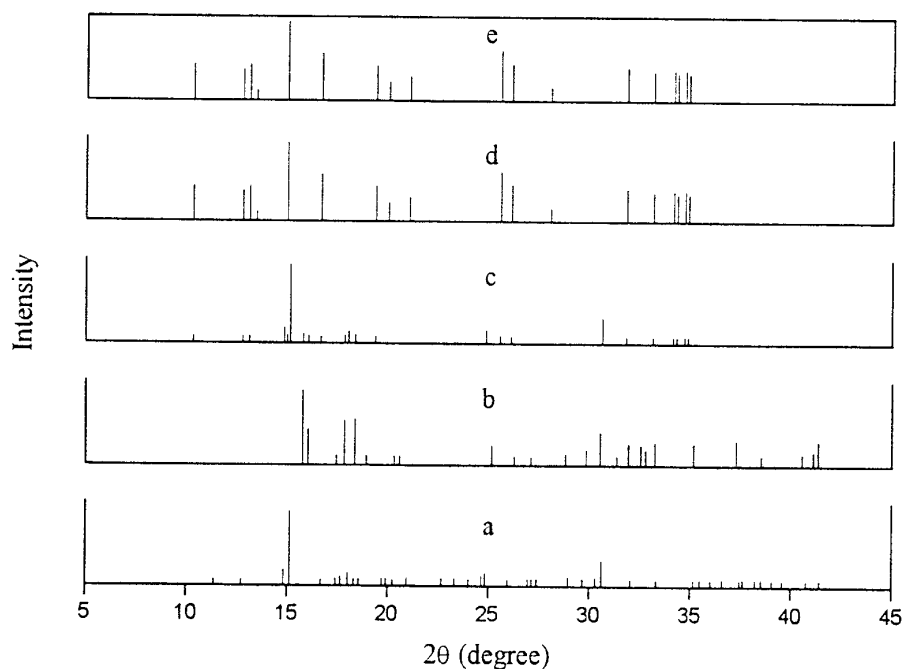
FIG. 1. XRD patterns: (a) 4-methylbenzenamine, (b) $NiCl_2 \cdot 6H_2O$, (c) the mixture in solid state after being ground for 5 min, (d) the mixture in solid state after being ground for 15 min, (e) $Ni(C_7H_9N)_2Cl_2$ prepared in solution (5).

In order to prove that the water of crystallization in our system did not play an important role in the reactions, the following experiments were also conducted:

The aqueous solutions of $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ were made up separately, and then the corresponding amount of 4-methylbenzenamine was immersed in them because 4-methylbenzenamine does not dissolve in water. After being allowed to stand for one day, the color of the aqueous solutions did not change and the amount of 4-methylbenzenamine did not decrease despite the solutions being stirred. The results which were contrary to the results in the nonaqueous solutions (3–5) illustrate the fact that the water did not participate in the reactions. While in the solid system the only possible solvent was the water of crystallization, the inference that the water of crystallization did not function as a solvent in the above reactions is self-evident.

RESULTS AND DISCUSSIONS

There are at least three clear possibilities for the slow, rate controling step in a heterogeneous solid state reaction: (a) transport of reactants to the reaction interface, (b) reaction at the interface, and (c) transport of products away from the reaction interface (7). In the above-mentioned system, both the grain size of the reactants and the reaction conditions, such as temperature and grinding rate are identical. Furthermore, there are many similarities among the reactants in the three substitution reactions (Table 1) besides the same incoming ligand, 4-methylbenzenamine. This rules out the possibility of step (a) which is determined mainly by the diffusion rate. As far as step (c), which has a relationship with the products, is concerned, the three reactions have much in common not only in releasing water but in the crystal structures of the solid products which show a

TABLE 1
The Similarities among $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $CuCl_2 \cdot 2H_2O$

Complex	$CoCl_2 \cdot 6H_2O$	$NiCl_2 \cdot 6H_2O$	$CuCl_2 \cdot 2H_2O$
Metal ionic radius (8) (Å)	0.72	0.70	0.72
Metal ionic charge	$+2$	$+2$	$+2$
Molecular structure	Transconfiguration octahedral (9, 10)	Transconfiguration octahedra (10)	Transconfiguration octahedral (10)
Space group (11)	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z(11)	2	2	2

TABLE 2
(A) The Activation Energy (ΔE_a) for Substitution Reactions Showing Octahedral Coordination with the Assumption of an S_{N_1} Mechanism

Electron configuration	LFSE[a] (Dq)		ΔE_a (Dq)
	Octahedron	Tetragonal pyramid	
	High spin		
d^7	-8	-9.14	-1.14
d^8	-12	-10.00	$+2.00$
d^9	-6	-9.14	-3.14

(B) The Activation Energy (ΔE_a) for Substitution Reactions Showing Octahedral Coordination with the Assumption of an S_{N_2} Mechanism

Electron configuration	LFSE[a] (Dq)		ΔE_a (Dq)
	Octahedron	Pentagonal pyramid	
	High spin		
d^7	-8	-10.56	-2.56
d^8	-12	-7.74	$+4.26$
d^9	-6	-4.93	$+1.07$

[a] LFSE, ligand field stabilization energy.

similarity in distorted octahedron (12, 13). Thus it could also be excluded from being the rate controling step of the substitution reaction. Reasonably, step (b) would be that which determines the reaction rates in this specific system.

It is highly probable that the above-mentioned analogies among the reactions exclude impact factors in molecular structure and ligand which could influence step (b). Thus kinetic stability of the transition metal complexes with regard to substitution reaction on the basis of their various electron configurations in the ligand field theory is considered to be the most important factor which decides the substitution rate in the above-mentioned system. From the quantitative information listed in Table 2 concerning the contribution of ligand field stabilization to the activation energy for substitution reactions of octahedral complexes (14), it is clear that Ni(II) whose electron configuration is d^8 possesses the largest positive ΔE_a value among the three reactants despite how the substitution reactions proceed according to an S_{N_1} mechanism whose assumed transition state is a tetragonal pyramid or to an S_{N_2} mechanism whose assumed transition state is a pentagonal bipyramid. However, the d^7 complex (Co^{2+}) has a negative value of ΔE_a by whichever reaction pathway it proceeds. As to the d^9

complex (Cu^{2+}), ΔE_a is negative when reaction occurs via an S_{N_1} mechanism while it is a smaller positive value when reaction occurs via an S_{N_2} mechanism. Since ΔE_a is the difference between the stabilization energy for the geometrical configuration corresponding to the transition state and the octahedral stabilization energy, the largest positive ΔE_a of the d^8 complex indicates that the octahedral configuration for Ni(II) is stable with respect to the geometrical configuration corresponding to the transition state, and the contribution to the activation energy is necessary. As is the case in the above discussions, the smaller positive or negative value of ΔE_a for Co(II) and Cu(II) means that the octahedral configuration for them was unstable with respect to the geometrical configuration corresponding to the transition state, and the contribution to the activation energy is virtually zero. Thus Ni(II) should likewise be inert in the substitution while Co(II) and Cu(II) should be labile in the reaction. In summary, the larger ΔE_a, the more slowly the substitution reaction should proceed. This is the result of our experiments, and it reveals the fact that the inert and labile phenomena in the substitution reactions exist in both solution and solid state.

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