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Reaction of 1,2-Dichloroethane with Pyridine Using the 1*R*,4*S*,8*R*,11*S*-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Cation as a Probe

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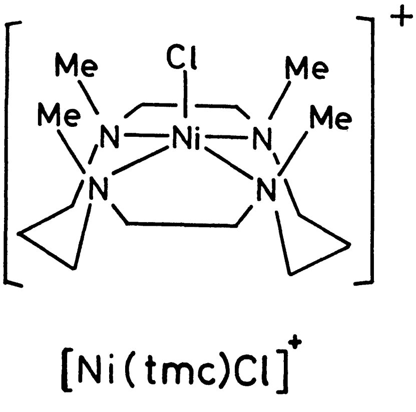
A spectral change of the title square planar cation $[Ni(tmc)]^{2+}$ by an axial ligation of the halide ions in nitrobenzene was applied to kinetic studies of pyridine and alkyl halides. The ligation of the chloride ions proceeds with a formation constant of more than 1×10^4 $dm^3 mol^{-1}$ and rapidly with a rate of less than millisecond. It was found that 1,2-dichloroethane and dichloromethane react with pyridine through the Menschutkin reaction with a rate constant of 1.2×10^{-8} and 3.7×10^{-9} $dm^3 mol^{-1} s^{-1}$ at 35 °C, respectively.

1,2-Dichloroethane (DCE) is a very useful solvent with a favorable boiling point, an intermediate dielectric constant and non-hydrogen-bonding property as an inactive medium for various reactions.

It is well known that the Menschutkin reaction occurs between amines and alkyl halides.[1-9] Nevstad and Songstad[3] examined the reactivity of dichloromethane (DCM) toward amines in DCM at 25 °C and found that the reaction rate of DCM-trimethylamine is considerable: the half-life (τ) is *ca.* 18 h, while pyridine (Py) reacts exceedingly slowly with DCM (τ=ca. 9600 h). On the other hand, no kinetic study has been reported for DCE, and this solvent is widely used without the special precautions at room temperatures. Gutmann[10,11] used DCE as a standard of basicity of solvents in which enthalpy of adduct formation of $SbCl_5$ with donor solvents was measured. However, it was pointed out that DCE rapidly quaternizes triethylamine under the catalytic action of $SbCl_5$.[12,13]

In the course of study of axial coordination of donor solvents to $[Ni(tmc)]^{2+}$ (tmc=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in DCE, the time-dependent spectra of the $[Ni(tmc)]^{2+}$ cation were observed when Py is present and it was found that the resultant spectrum is referred to the chloride coordinated $[Ni(tmc)Cl]^+$ cation (Scheme 1), showing the occurrence of the Menschutkin reaction between Py and DCE. Usually, the Menschutkin reaction has been examined by using conductometry and the silver nitrate titration. In this work the reaction between Py and alkyl halides in nitrobenzene (NB) as solvent was studied kinetically by using the square planar $[Ni(tmc)]^{2+}$ cation which shows color change from red to blue by an axial ligation of the halide ion.



[Ni(tmc)Cl]⁺

Scheme 1.

Experimental

The salt $[Ni(tmc)](ClO_4)_2$ with (1*R*,4*S*,8*R*,11*S*)-nitrogen configuration was prepared by the published method[14,15] and was recrystallized from acetone-diethyl ether mixtures. Purity of the salt was checked by elemental analysis and IR spectra. Tetraphenylphosphonium bromide was prepared by the reported method[16] and the crude product was recrystallized by the method described previously.[17] Tetraphenylphosphonium chloride and tetraethylammonium chloride (Wako Pure Chemical Industries Ltd.) were recrystallized from an acetone-ether mixture. Purification of Py, DCE, and NB has been described previously.[18,19] Bromoethane (BE) of reagent grade (Wako Pure Chemical Industries Ltd.) was purified by fractional distillation through a 1.2-m column without washing.

The instrumentation and the procedure used for measurements of spectra and conductance were the same as described previously.[19]

Results and Discussion

In Fig. 1 are shown the spectra of $[Ni(tmc)](ClO_4)_2$ in a Py-DCE mixed solvent at 25 °C which change with time. The absorption peak at 524 nm is assigned to the low-spin, square planar species and the peaks at 430 nm and 720 nm to the high-spin, square pyramidal species. It is clearly shown that a certain ligand which is generated with the passage of time is coordinated to form a square pyramidal species. In our previous study,[19] it was found that neither DCE nor Py are coordinated because the basicity of DCE is too low and coordination of Py is sterically hindered in spite of its high basicity. If water is contained in their mixture, water molecules hydrogen-bonded to Py can be coordinated because of

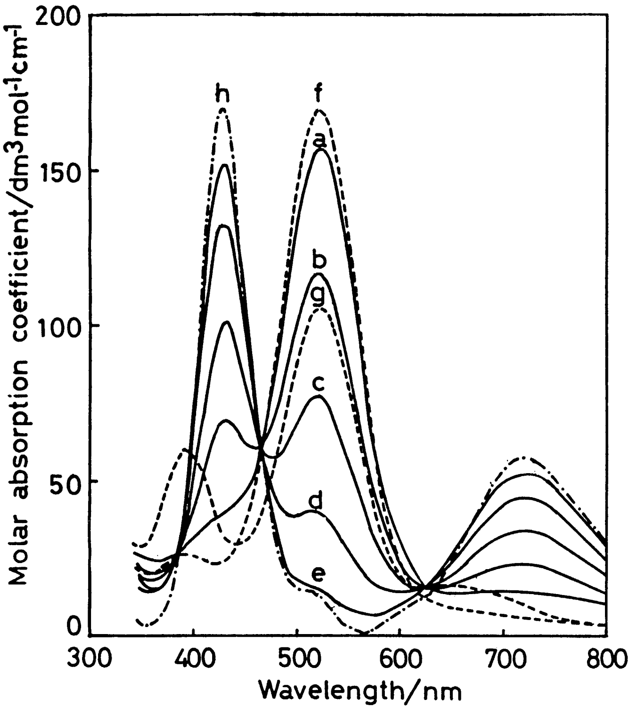


Fig. 1. Visible spectrum variation of a 1×10^{-3} mol dm^{-3} solution of $[Ni(tmc)](ClO_4)_2$ with time and water contents in Py at 25 °C. The DCE molar fraction (0.19): a, 16 min after preparation of the solution; b, 46; c, 76; d, 106; e, 136. Without DCE: f, $[H_2O]=8.6\times10^{-3}$ mol dm^{-3}; g, 5.7×10^{-2}. h, Spectrum of $[Ni(tmc)Cl]ClO_4$ in Py.

the increased basicity of water by polarization through hydrogen-bonding.[20,21] But as shown in Fig. 1, the water-coordinated species has an isosbestic point at 607 nm and absorption peaks at 390 nm and 660 nm, different from the time-dependent spectrum. Therefore, coordination of another ligand should be considered.

Alkyl halides react with amines, that is the Menschutkin reaction, forming quaternary ammonium salts with halide ions, and several works concerning this reaction of Py and alkyl halides at both atmospheric and elevated pressures have been reported.[6–9] As far as we know, however, reactivity of DCE with amines has not been examined in spite of the fact that DCE is very widely used as various reaction media.

The salt $[Ni(tmc)Cl]ClO_4$ was prepared by adding an equivalent sodium chloride to the aqueous $[Ni(tmc)](ClO_4)_2$ solution[14] and its spectrum was recorded ((h) in Fig. 1). The time-dependent spectrum which has absorption peaks at 430 nm and 720 nm coincides with that of the chloride-coordinated species. Therefore, it can be said that DCE reacts with Py to form quaternary ammonium chloride as depicted by Eq. 1. If the resultant chloride ion is

$$ClCH_2CH_2Cl + NC_5H_5 \longrightarrow ClCH_2CH_2N^+C_5H_5\ Cl^- \quad (1)$$

determined, the rate of reaction can be evaluated.

Coordination of the Chloride and Bromide Ions to $[Ni(tmc)]^{2+}$. The first ionic association constant of $[Ni(tmc)]^{2+}$ with the ClO_4^- ion is 1190 dm^3 mol^{-1} [19] in NB which indicates that 49% of $[Ni(tmc)]^{2+}$ are associated with ClO_4^- at 0.001 mol dm^{-3}. The association results from electrostatic attractive forces because of the weak basicity of ClO_4^- and the nickel complex cation remains the four-coordinated species. When a more basic solute is present, its coordination is hardly interrupted by the perchlorate association.[19]

Coordination of the chloride and bromide ions was examined spectrophotometrically by adding tetraphenylphosphonium or tetraethylammonium chloride and tetraphenylphosphonium bromide to the $[Ni(tmc)](ClO_4)_2$ solutions. Table 1 gives variation of the molar absorption coefficient (ε) of the complex cation at 524 nm with the concentration of chloride and bromide ions in DCE–NB mixed solvents. It was found that the ε values decrease linearly with increasing the halide ion concentration. The formation constant K_{NiX} was calculated by equation

$$K_{NiX}=(\varepsilon_o-\varepsilon)/(\varepsilon-\varepsilon_s)[X^-], \quad (2)$$

where ε_o is the molar absorption coefficient of the four-coordinated species at 524 nm and ε_s is the molar absorption coefficient of the five-coordinated species (ε_s=10 dm^3 mol^{-1} cm^{-1} [19]). $[X^-]$ is the concentration of the non-coordinated halide ion. The K_{NiX} values obtained are given in the last column. The activity

Table 1. Coordination of the Chloride and Bromide Ions to $[Ni(tmc)]^{2+}$ at 35 °C

X_{DCE}	Salt	$[X^-]$	$[[Ni(tmc)]^{2+}]$	ε_o	ε	K_{NiX}
		10^{-4} mol dm^{-3}	10^{-3} mol dm^{-3}	dm^3 mol^{-1} cm^{-1}		10^4 dm^3 mol^{-1}
0	Ph_4PBr	0.755	0.983	209	195	1.2
0		2.05	0.970	209	171	1.2
0.10	Ph_4PCl	1.05	1.02	207	188	1.7
0.10		1.83	1.01	207	174	1.4
0.40	Et_4NCl	4.41	1.02	199	119	7.9
0.40	Ph_4NCl	2.36	1.00	199	155	9.5
0.40		5.35	0.975	199	98	8.2

coefficient is not taken into account because a constant $[Ni(tmc)]^{2+}$ concentration of *ca.* 1×10^{-3} mol dm^{-3} was used throughout the work. It is seen that the formation constant is one order of magnitude larger than the ionic association constant for the perchlorate ion and an increase in DCE molar fraction strengthens the coordination of halide ions. The rate of coordination of Cl^- ions to $[Ni(tmc)]^{2+}$ could not be measured by the stopped-flow method, showing that it is faster than millisecond. The results obtained above show that the $[Ni(tmc)]^{2+}$ cation can be used as a probe for the Menschutkin reaction.

Estimation of the Rate Constant of the Menschutkin Reaction. For the Menschutkin reaction the second-order rate equation Eq. 2 applies,

$$dx/dt = k_2(a-x)(b-x), \tag{3}$$

and then it is rewritten as

$$\ln(b-x)/(a-x) = (b-a)k_2t - \ln a/b \tag{4}$$

where k_2 is the rate constant in dm^3 mol^{-1} s^{-1} and a and b are the initial concentrations of alkyl halide and Py, respectively, and x is the concentration of the product (ammonium salt) formed after an interval of t s. The x values are estimated by using the coordination constant K_{NiX}

$$x = m'[1 + 1/K_{NiX}(m-m')] \tag{5}$$

where m' is the concentration of five-coordinated species, and m is the initial concentration of four-coordinated species. Since the K_{NiX} values are more than 10^4 and so the contribution of the second term in Eq. 5 is very small, the K_{NiX} value in Table 1 in the solvent composition close to the solvent system in question was used for calculation.

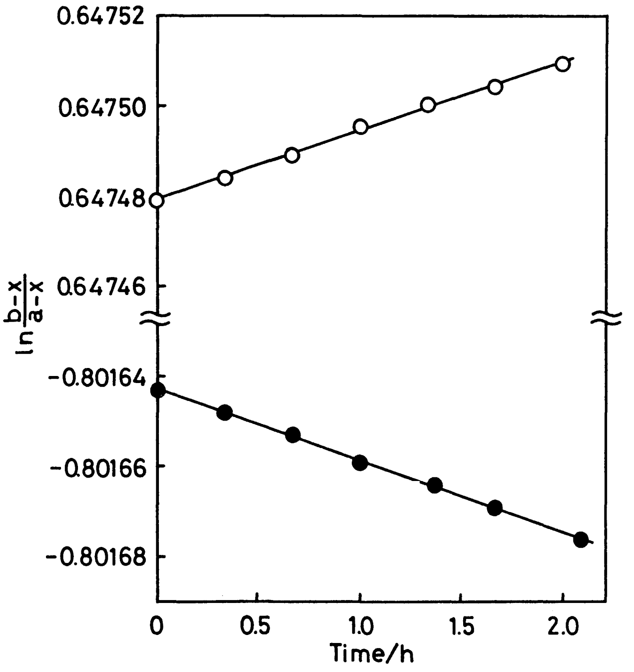


Fig. 2. Plots of $\ln(b-x)/(a-x)$ vs. t in NB at 35 °C. [DCE], [Py] in mol dm^{-3}: a, 0.411, 0.786; b, 0.844, 0.379.

Typical examples of plot of Eq. 4 for the DCE-Py system in NB are illustrated in Fig. 2. Good linear relationships were obtained from which the k_2 rate constants were calculated. Similar measurements were made as a reference in the DCE-NB mixture without Py and in the Py-NB mixture without DCE, and it was confirmed that the change in absorbances is negligible compared with that in the DCE-Py system.

Table 2. Second Order Rate Constants for the Reaction of Py with DCE, DCM, and BE in NB at 35 °C

[Py] mol dm^{-3}	[DCE] mol dm^{-3}	k_2 10^{-8} dm^3 mol^{-1} s^{-1}
0.0924	1.12	1.1
0.143	1.03	1.1
0.258	0.958	1.1
0.379	0.844	0.92
0.786	0.411	1.1
0.807	0.206	1.4
0.877	0.243	1.1
0.446	5.50	0.68
0.503	5.55	0.64
0.886	5.22	0.64
1.39	5.16	0.59
1.52	4.47	0.63
2.01	4.08	0.63
2.52	3.89	0.62
3.80	2.48	0.70
3.91	1.96	0.69
4.49	1.56	0.72
4.93	0.919	0.80
5.01	1.29	0.71
5.53	0.506	0.85
10.0	2.41	0.26[a)]
11.4	1.02	0.27[a)]
12.3	0.112	1.1[a)]
[Py] mol dm^{-3}	**[DCM] mol dm^{-3}**	**k_2 10^{-9} dm^3 mol^{-1} s^{-1}**
0.109	0.911	2.6
0.267	0.859	2.5
0.317	0.710	2.5
0.801	0.227	3.1
0.912	0.0974	3.8
[Py] mol dm^{-3}	**[BE] mol dm^{-3}**	**k_2 10^{-5} dm^3 mol^{-1} s^{-1}**
0.00593	0.139	1.1
0.0240	0.116	1.0
0.0274	0.0860	1.1
0.0336	0.0415	1.1
0.0662	0.0196	1.1
0.0736	0.0325	1.1
0.0903	0.00636	1.3
0.112	0.00225	1.1
0.134	0.0103	1.1
0.137	0.00527	1.1

a) Obtained without NB at 25 °C.

The k_2 values obtained in this way are summarized in Table 2.

The conductance measurements were also carried out to evaluate the k_2 value in a different method. Figure 3 typically shows variation of the conductivity with time in a reactant composition of [DCE]=0.826 mol dm^{-3} and [Py]=0.413 mol dm^{-3} in NB at 35 °C. The chloride and bromide concentrations were approximately evaluated by using the molar conductance of tetraphenylphosphonium chloride and bromide, respectively because the corresponding salts are not available.

Figures 4 and 5 show the dependence of k_2 values obtained spectrometrically and conductometrically on the DCE fraction. A slight difference is found for conductometry, this being because the salts using for calibration are not the same as the products. It is seen that for DCE the rate constant slightly increases with decreasing the DCE fraction. This may be due to the secondary Menschutkin reaction of the DCE molecule having two reaction sites leading to the *N*,*N*-ethylenedipyridinium cation $H_5C_5N^+CH_2CH_2N^+C_5H_5$, in view of the fact that such dependence was not observed for BE having one reaction site. The conductance results show the same trends. In the case of the greater content of more polar NB as the diluent, that is, the lower concentration of reactants, the rate constant is large, reflecting the ionic product in the Menschutkin reaction.

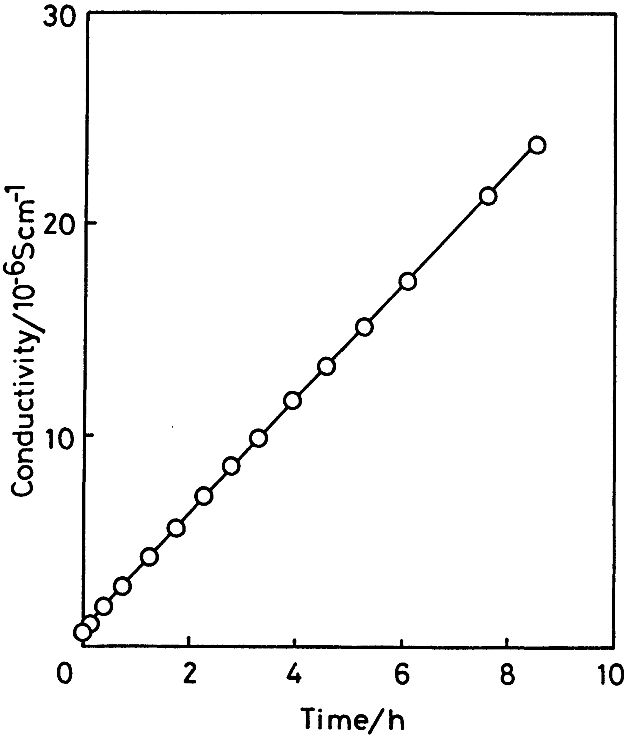


Fig. 3. Variation of the conductivity for [Ni(tmc)](ClO$_4$)$_2$ with time in NB at 35 °C. [DCE]=0.826 mol dm^{-3}, [Py]=0.413 mol dm^{-3}.

Table 3 gives the rate constants according to spectrophotometry extrapolated to zero concentration of Py at which the 1 : 2 DCE–Py reaction is negligible. The rate of reaction for DCM is one order of magnitude smaller than that for DCE, DCM being a little more stable than DCE. Maria and Gal[22] pointed out

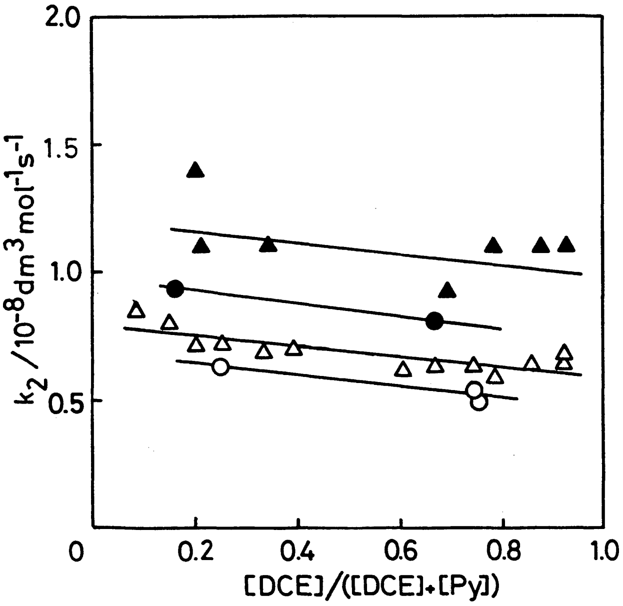


Fig. 4. Variation of the rate constant for the DCE–Py system with the DCE molar fraction in NB at 35 °C. The total concentration of DCE and Py is *ca.* 1.1 mol dm^{-3}: ▲, spectrometry; ●, conductometry. The total concentration is *ca.* 6 mol dm^{-3}: △, spectrometry; ○, conductometry.

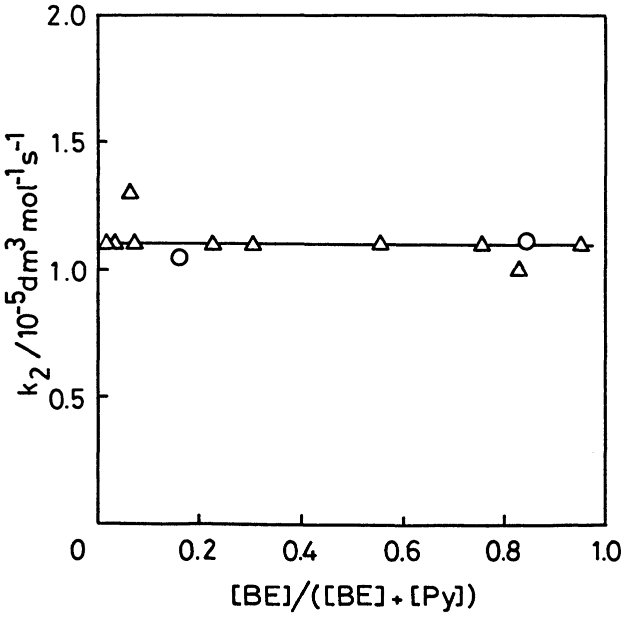


Fig. 5. Variation of the rate constant for the BE–Py system with the BE molar fraction in NB at 35 °C. △, spectrometry; ○, conductometry.

Table 3. Extrapolated Second Order Rate Constants for the Reaction of Py with DCE, DCM, and BE in NB at 35 °C

Halogeno-solvent(S)	k_2 / $dm^3\,mol^{-1}\,s^{-1}$	Initial concentration ([Py]+[S])/mol dm^{-3}
DCE	1.0×10^{-8}	1.0—1.2
	5.9×10^{-9}	5.9—6.5
DCM	2.2×10^{-9}	1.0—1.1
	$5\ \times10^{-10}$ a)	—
BE	1.1×10^{-5}	0.075—0.26
	8.8×10^{-6} b)	0.12

a) Measured in DCE at 25 °C. From Ref. 3. b) From Refs. 4 and 5.

that a non-negligible amount of charged species is contained in some DCE solutions of $SbCl_5$ and strong basic solute, and instead of DCE they used DCM as the solvent to establish a solvent Lewis basicity scale.

It can be concluded that although the rate of reaction is small, DCE surely reacts with Py through the Menschutkin reaction without the catalytic action of $SbCl_5$: the concentration of the chloride ions in the DCE-Py mixture amounts to 10^{-4} mol dm^{-3} level in 30 min at 25 °C.

The conductometry for the determination of halide ions suffers one disadvantage which is the difficulty in calibrating the conductivity of the salt generated in the Menschutkin reaction. The silver titration method is somewhat troublesome because it contains the procedure of extraction of the halide ions into an aqueous phase.3) On the other hand, the present system cannot be used when the basic, coordinating solvents such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, acetonitrile and water are present in the reaction system.19) However, if such basic solvents are not, the Menschutkin reaction can be easily monitored by the spectral change of the square planar $[Ni(tmc)]^{2+}$ cation without relying on conductometry or the silver titration method.

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