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Hydrogenation of Arenes with Metallic Iridium and Rhodium Powders Prepared from Iridium(I) and Rhodium(I)-COD Complexes under Mild Conditions

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Metallic iridium and rhodium powders prepared from the reactions of $[M(\text{COD})(\text{PhCN})_2]\text{ClO}_4$ ($M = \text{Ir}(1), \text{Rh}(2)$; COD = 1,5-cyclooctadiene) with hydrogen at room temperature in methylene chloride show catalytic activities for hydrogenation of arenes at room temperature under atmospheric pressure of hydrogen. Most substituents (CH_3 , COOH , NO_2 , CH_2OH , CHO , OPh , OCH_3 , $\text{C}=\text{C}$, halogens and CH_2Cl) on aromatic ring suppress the rate of the hydrogenation of the aromatic ring while the aromatic ring hydrogenation of phenol and 1,4-dihydroxobenzene is faster than that of benzene over these metallic powders. Hydrogenation of benzoic acid occurs only at the aromatic ring leaving the COOH group intact over iridium metal powders while benzoic acid is not hydrogenated at all over rhodium metal powders. Carbonyl, nitro, acetylenic and olefinic groups on an aromatic ring are hydrogenated prior to the aromatic ring hydrogenation. Hydrogenolysis of OH groups of phenol, benzyl alcohol and 1,4-dihydroxobenzene, and hydrodehalogenation of halobenzenes, benzyl halides and cinnamyl chloride also occur along with the hydrogenation of aromatic ring.

Introduction

Metallic powders and metal oxides are somewhat common heterogeneous catalysts.¹ Unsupported metallic catalysts are usually prepared by the reduction of metal compounds at high temperature under hydrogen mostly in the absence of a solvent or soaking in solution.² The characteristics of the unsupported metal surfaces have been recently investigated,³⁻⁷ and only a few reports have been made for the catalysis with unsupported metal powders^{2,8,9} while supported metallic catalysts are widely studied probably because they show high reactivities for small molecules such as CO , H_2 , O_2 , ethylene and other organic compounds.^{2,10-14}

Rhodium¹⁵ and iridium^{3,8,16} metallic powders have been generally obtained by the reduction of their chloride salts, $\text{M}(\text{III})\text{Cl}_3$ ($M = \text{Rh}, \text{Ir}$) under hydrogen at high temperature. Whitesides reported that platinum black is produced from the reaction of $\text{Pt}(\text{II})\text{-COD}$ (COD = 1,5-cyclooctadiene) complexes.⁹ Crabtree observed that $\text{Ir}(\text{I})\text{-COD}$ complexes under catalytic hydrogenation conditions show a strong resemblance to heterogeneous catalysts such as colloidal metallic iridium.^{17,18}

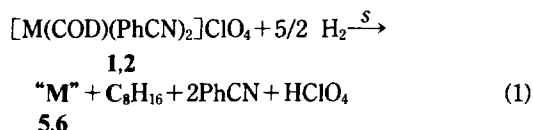
Catalytic hydrogenation of arenes and heteroarenes has

been studied with soluble metal compounds^{19,20} and heterogeneous catalysts^{1,21} such as metal powders, metal oxides, and supported metal complexes. Only one report, to our knowledge, has been made for the hydrogenation of benzene with iridium metal powders supported on metal oxides that were prepared under hydrogen at high temperature,^{16b} while extensive studies have been carried out for the hydrogenation of arenes with various metal powders supported and unsupported.^{1,19,21}

During the investigation of reactions of $\text{Ir}(\text{I})\text{-COD}$ complexes,²² we found that solutions of $[M(\text{COD})(\text{PhCN})_2]\text{ClO}_4$ ($M = \text{Ir}(1), \text{Rh}(2)$) under atmospheric pressure of hydrogen rapidly produce fine particles of iridium and rhodium metal at room temperature. This observation prompted us to look into the catalytic activities of these metal powders, and the hydrogenation of arenes was chosen to be investigated since iridium metal powders have never been extensively studied for their catalytic activities for the hydrogenation of arenes with various types of substituents. Iridium and rhodium metal powders (prepared under the same experimental conditions) show some differences in their catalytic activities, which are also included in this report.

Results and Discussion

Preparation of Metallic Iridium and Rhodium Powders. Reactions of $[M(\text{COD})(\text{PhCN})_2]\text{ClO}_4$ ($M=\text{Ir}(1), \text{Rh}(2)$) with hydrogen (1 atm) in methylene chloride (or methanol) at 0-100 °C produce fine metallic powders of iridium and rhodium (Eq. 1). (It should be mentioned that PhCN dissociated from **1** and **2** may be hydrogenated to give PhCH_2NH_2 and further to $\text{C}_6\text{H}_{11}\text{CH}_2\text{NH}_2$ with longer reaction time.) Formation of iridium powders from **1** is much faster than that from the reaction of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$, **3** in MeOH under the same experimental conditions while the production of rhodium powders from **2** is only slightly faster than that from $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, **4**.



$M=\text{Ir}(1), \text{Rh}(2)$; $s=\text{CH}_2\text{Cl}_2, \text{MeOH}$

"M" = metallic iridium (**5**) and rhodium (**6**) powders

C_8H_{16} = cyclooctane

Precipitation of metallic powders from **1** and **2** is faster in MeOH than in CH_2Cl_2 and becomes faster at higher temperature in both solvents. The formation of metallic powders becomes slower in the presence of excess substrates such as PhCN, PhCH_2NH_2 and PhCHO which can be hydrogenated by metallic powders to give PhCH_2NH_2 (further to $\text{C}_6\text{H}_{11}\text{CH}_2\text{NH}_2$), $\text{C}_6\text{H}_{11}\text{CH}_2\text{NH}_2$ and PhCH_2OH (further to $\text{C}_6\text{H}_{11}\text{CH}_2\text{OH}$), respectively. The reaction of **1** in the solid state with H_2 (1 atm) also produces iridium powders and cyclooctane.^{22b} Rhodium powders are also obtained from the reaction of **2** in the solid state with H_2 with much slower rate.

Both EDX and ESCA measurements show no signals due to metal oxides in the samples of metallic powders prepared in this study. Scanning electron microscope measurements show spherical particles of metal powders with diameters in the range of 0.05-0.6 μm depending upon the experimental conditions for the production of metal powders. Particle size measurements by dynamic laser light scattering method also gave practically the same results (see Figure 1). Catalytic activities (rates of hydrogenation of arenes) of metallic powders prepared in this study vary significantly depending on the conditions under which the powders are prepared. Iridium and rhodium powders prepared in methylene chloride show higher catalytic activities (hydrogenation rates) than do those obtained in methanol under the same experimental conditions.²³ The particle size of metals increases as the reaction time becomes longer (see Figure 1). Those particles smaller than 0.05 μm of diameter (produced at 25 °C in methylene chloride for less than 3 hours) are pyrophoric and need special precautions for handling. Therefore, larger iridium powders (*ca.* 0.5 μm in diameter, see Figure 1) prepared in methylene chloride at 25 °C for 6 hours under 1 atm of hydrogen were used in this study. Rhodium powders used in this study were obtained under the same experimental conditions and are somewhat larger (*ca.* 0.75 μm).

Catalytic Hydrogenation of Arenes. Table 1 summarizes the results for the hydrogenation of arenes with iridium

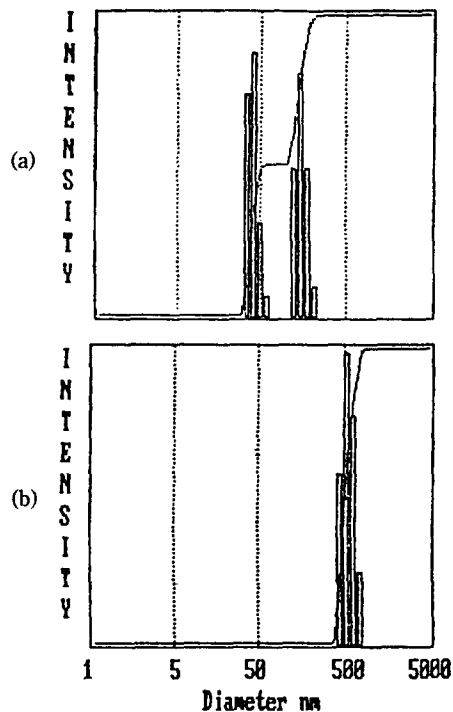


Figure 1. Particle Size Distribution of Metallic Iridium Powders (**5**) obtained from the Reactions of $[\text{Ir}(\text{COD})(\text{PhCN})_2]\text{ClO}_4$ (**1**) with H_2 (1 atm) at 25 °C in CH_2Cl_2 (a) for 3 Hours and (b) 6 Hours, measured by Dynamic Laser Scattering method at 25 °C in CH_2Cl_2 .

powders, **5** obtained from **1**. Rates of the hydrogenation of arenes shown with metallic rhodium powders, **6** obtained from **2** are in general considerably slower than those with iridium powders, **5** and not given in Table 1. The catalytic hydrogenation with the metallic iridium, **7** and rhodium, **8** powders obtained from **3** and **4** are in general much slower than that with **5** and **6**, respectively, obtained under the same experimental conditions.

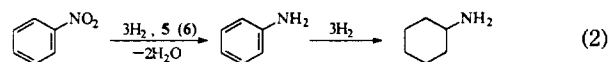
Hydrogenation of benzene is significantly faster than that of methylbenzene with the metallic iridium, **5** and rhodium, **6** powders (Table 1) as observed with a soluble rhodium(I) complex^{19c} and rhodium(I) complexes supported on phosphinated polyacetylene and silica.^{21b}

Hydrogenation of benzoic acid with iridium powders, **5** gives cyclohexane carboxylic acid leaving the carboxylic group intact while most functional groups on aromatic ring react with H_2 on iridium powders, **5** (see Table 1). Neither the aromatic ring nor carboxylic group of benzoic acid is hydrogenated on rhodium metallic powders, **6** at 25 °C under atmospheric pressure of H_2 .

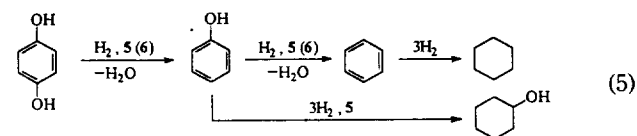
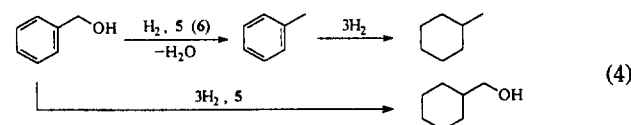
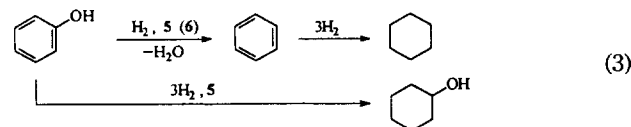
The nitro group of nitrobenzene seems to be hydrogenated prior to the hydrogenation of the aromatic ring over **5** and **6** (Eq. 2) since aniline was seen at the early stage of the reaction and then disappeared (see Table 1) as benzene began to be seen. Selective hydrogenation of nitro group on an aromatic ring has been reported with $\text{Ir}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ ²⁴ and PtO_2 , carbon-supported Pd, PdCl_2 and alumina supported Rh.²⁵

Table 1. Hydrogenation of Arenes with Metallic Iridium Powders, **5** (see Experimental for preparation and text for physical properties) at 25 °C under 1 atm of hydrogen in CDCl₃

Substrate	Products	S/Ir/hr ^a	Remarks
		0.4	
		0.1	
		0.1	
		0.08	
		0.17	/ = 0.56
		0.11	/ = 0.56
		0.59	/ = 1.2
		0.6	/ = 2.2
		0.22	/ = 0.8
		0.1	
		0.1	-CH=CH ^b -CH ₂ CH ₃ ^b
		0.04	-CH=CH- ^b -CH ₂ CH ₃ - ^b
		0.003	-CO ₂ CH ₂ - ^b -CO ₂ CH ₂ - ^b
		0.11	
		0.03	
		0.10	
		0.09	-C ₂ H ₇ / -C ₂ H ₄ Cl = 2.4

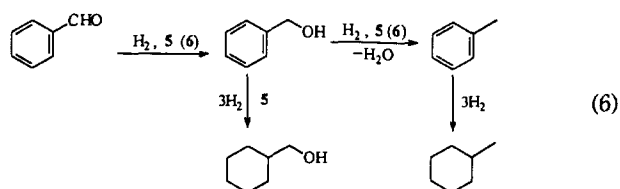
^a Reaction rate, substrate molecules/Ir atom/hour.^b Observed initially and disappeared.

Hydrogenation of the aromatic rings of phenol, benzyl alcohol and 1,4-dihydroxobenzene seems to occur simultaneously with the hydrogenolysis of the hydroxo groups in the presence of the iridium metal powders, **5** while the hydrogenolysis of the hydroxo groups (*e.g.*, phenol to benzene) always occurs prior to the ring hydrogenation in the presence of the rhodium powders, **6** (see Eq. 3-5). It is somewhat surprising not to see cyclohexanol and cyclohexylmethanol only when the rhodium powders, **6** are used as catalyst (see Eq. 3-5). In separate experiments, it has been found that neither cyclohexanol and nor cyclohexylmethanol reacts with H₂ over **5** and **6**: once the aromatic rings of phenol, benzyl alcohol and 1,4-dihydroxobenzene are hydrogenated, then the hydroxyl groups of cyclohexanol and cyclohexylmethanol do not undergo the hydrogenolysis. Cyclohexane and methylcyclohexane (in Table 1 and Eq. 3-5) are then the hydrogenation products of benzene and methylbenzene produced in the hydrogenolysis of phenol, benzyl alcohol and 1,4-dihydroxobenzene. Similar results have been reported both in homogeneous and heterogeneous catalysis: catalytic hydrogenolysis of unsaturated alcohols has been observed in the presence of soluble iridium(I) complexes,²⁶ Pd Rh supported on carbon²⁷ which are not catalytically active for the hydrogenolysis of saturated alcohols. These observations suggest an important role of aromatic ring close OH group for the hydrogenolysis (cleavage of C-OH bond).

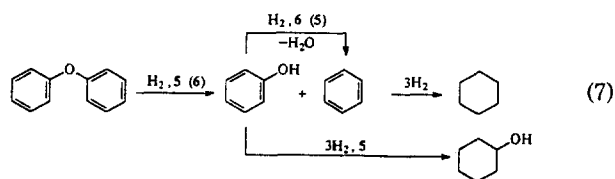


The aldehyde group of benzaldehyde seems to be hydrogenated to give benzyl alcohol before the aromatic ring hydrogenation occurs (Eq. 6) since significant amounts of benzyl alcohol and methylbenzene were initially observed and disappeared in the presence of **5** and **6**. It was clearly seen that both of cyclohexylmethanol and methylcyclohexane are produced at the expense of benzyl alcohol and methylbenzene in the presence of **5** according to the ¹H NMR spectral changes during the reaction. Cyclohexylmethanol, however, has not been measured in the presence of **6** (*cf.* Eq. 3). Cyclohexyl aldehyde was never observed during the hydrogenation of benzaldehyde in the presence of **5** and **6**. Carbonyl group hydrogenation has been reported with soluble iridium

complexes²⁸ and various metals as heterogeneous catalysts²⁹ while no report has been made, to our knowledge, with iridium metal.

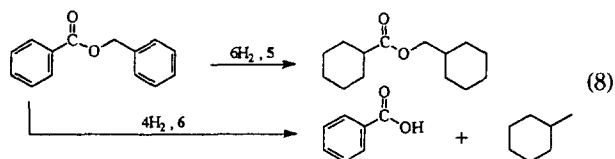


Diphenyl ether, in the presence of **5** and **6** under hydrogen, seems to initially undergo C-O bond cleavage to give phenol and benzene although phenol and benzene were not observed during the catalysis (Eq. 7). The product ratio (cyclohexanol/cyclohexane=0.8 and 0 with **5** and **6**, respectively) clearly suggests the initial C-O bond cleavage followed by phenyl ring hydrogenation. The product ratio should be 1.0 if the hydrogenation occurred before the C-O bond cleavage since dicyclohexyl ether does not react with H₂ in the presence of **5** and **6**. In the presence of **5**, phenol is then hydrogenated to give cyclohexanol or undergoes the hydrogenolysis followed by hydrogenation to give cyclohexane while in the presence of **6**, only cyclohexane is seen (Eq. 7) as observed above (Eq. 3 and 5). Methanol is produced from the hydrogenolysis of methylphenyl ether in the presence of **5** while cyclohexanol has not been observed (see Table 1), which may suggest that the C-O bond cleavage occurs preferably to the C (aromatic carbon)-O bond rather than the C (aliphatic carbon)-O bond.

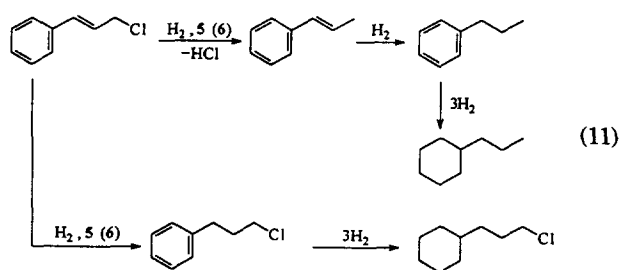
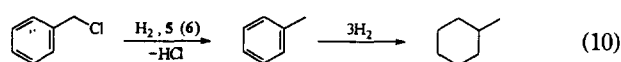
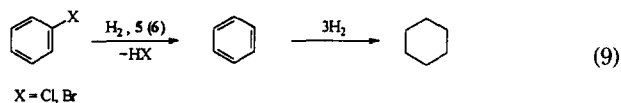


Hydrogenation of benzyl benzoate (PhCO₂CH₂Ph) reveals a striking difference in catalytic activities between the iridium and rhodium metal powders prepared in this study. The two phenyl rings of benzyl benzoate are slowly hydrogenated one by one to give C₆H₁₁CO₂CH₂C₆H₁₁ leaving -C(O)O- group intact in the presence of iridium powders, **5** (Eq. 8). One phenyl ring hydrogenation products (C₆H₁₁CO₂CH₂Ph and PhCO₂CH₂C₆H₁₁) were measured at the early stage of the reaction and then disappeared to give C₆H₁₁CO₂CH₂C₆H₁₁. In the presence of rhodium powders, **6** on the other hand, benzyl benzoate undergoes O-CH₂ bond cleavage to give benzoic acid and methylbenzene, among which only methylbenzene is hydrogenated to give methylcyclohexane (Eq. 8).

The intermediate products given in Table 1 for the hydrogenation of phenylacetylene and diphenylacetylene with **5** suggest the initial hydrogenation of the C≡C group followed by C=C group hydrogenation and then finally the aromatic ring hydrogenation.



Reactions of phenyl, benzyl and cinnamyl halides with H₂ over the iridium, **5** and rhodium, **6** powders seem to initially give hydrodehalogenation products which are then further hydrogenated to give saturated cyclohydrocarbons (see Eq. 9-11 and Table 1). Hydrodehalogenation of chloroarenes was reported before with soluble rhodium complexes.³⁰ The hydrodehalogenation of halobenzenes and benzyl halide seems to occur prior to the hydrogenation of aromatic ring (Eq. 9 and 10) since cyclohexane was never found in the separate reactions of chlorocyclohexane with H₂ in the presence of **5** and **6**. With the iridium powders, **5** the hydrodehalogenation is faster for chlorobenzene than for bromobenzene (see Table 1). It was previously reported that chlorobenzene undergoes the hydrodehalogenation faster than does fluorobenzene in the presence of RhCl₃-aliquot-336.³¹ The fact that chlorocyclohexane and 3-cyclohexylpropyl chloride do not undergo any reaction under H₂ over **5** suggests important roles of aromatic ring and olefinic group close to halogen atom for the hydrodehalogenation (carbon-halogen bond cleavage). Vinylic and allylic halides without an aromatic ring close to halogen atom are known to undergo only the hydrogenation to give haloalkanes with metallic rhodium supported on alumina.³² Four chlorines of 2,3,4,5-tetrachloroaniline have been removed one by one with palladium metal supported on carbon.³³



Experimental

Caution. Extensive precautions should be taken in handling perchlorate salts and perchlorato complexes of transition metals since they are potentially explosive.³⁴

Materials. Metal(III) chloride hydrate, IrCl₃·xH₂O and RhCl₃·xH₂O were purchased from Aldrich Chemicals (20624-5/Ir and 20626-1/Rh) and Strem Chemicals (77-3000/Ir and 45-1850/Rh), and the chemicals from the two companies showed no significant differences in the formation and catalytic activities of metallic powders. M(I)-COD complexes, [M(COD)Cl]₂ and [M(COD)(PhCN)₂]ClO₄ (M=Ir, Rh) were prepared by the literature methods.^{35,36} All the arenes were reagent grade and used as purchased from Aldrich and Fluka. All solvents were purified by standard methods before use.

Instruments. ¹H NMR spectra were recorded on a Varian Gemini 300 and Varian EM-360 spectrometer at 300 and 60 MHz. A Varian 3700 and Hewlett Packard HP 5890A

gas chromatograph were used for analysis of reaction mixtures. A Jeol JSM-840 and Esca Lab MKII (VG Scientific Ltd.) (Lucky Research Center) were used for SEM and ESCA measurements. Particle size analysis was performed using dynamic laser light scattering method in CH_2Cl_2 at Prof. H. Lee's laboratory at Chem. Dept., Sogang University.

Preparation of Metallic Iridium and Rhodium Powders a) from the Solutions of $[\text{M}(\text{COD})(\text{PhCN})_2]\text{ClO}_4$.

Addition of AgClO_4 (0.3 mmol, 62 mg) into red CH_2Cl_2 solution (5 mL) of $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.15 mmol, 100 mg) in the presence of PhCN (0.6 mmol, 0.07 mL) under nitrogen at 25 °C resulted in precipitation of white AgCl and yellow solution within 30 min. (Reactions of $[\text{M}(\text{COD})\text{Cl}]_2$ (M=Ir, Rh) with AgClO_4 in the presence of RCN are known to give $[\text{M}(\text{COD})(\text{RCN})_2]\text{ClO}_4$ [36].) AgCl was removed by filtration and the solution was stirred under H_2 (1 atm) at 25 °C for 6 hours during which time the yellow solution gradually turned black colloidal suspension. Black iridium metallic powders, **5** (ca. 50 mg) were separated by centrifuge and washed with methanol (5 mL) several times and dried in vacuum. Rhodium powders, **6** were prepared in the same manner as described above for **5**.

b) from the Solutions of $\text{MCl}_3 \cdot x\text{H}_2\text{O}$ (M=Ir, Rh).

Metallic powders of iridium, **7** and rhodium, **8** were prepared in the same manner as described above for **5** except that MeOH was used as a solvent.

Catalytic Hydrogenation of Arenes. In most experiments, the mole ratio of an arene to metal was kept to be 15. The reaction mixture of an arene (1.13 mmol) and metal powders (0.073 mmol) in CDCl_3 (10 mL) was stirred under 1 atm of H_2 at 25 °C for certain period of time. A part of reaction mixture (0.5 mL) was taken out of the reactor at the interval and the insoluble metal catalyst was removed by centrifuge before analyzing the reactant and products. ^1H NMR spectral measurements were employed for the analysis of reactants and products for the reactions of such as benzene, methylbenzene and halobenzenes where the reactants and products can be separately identified by the signals. For the reactions of the arenes for which the reactants and products can not be analyzed simply by measuring the ^1H NMR spectra of the reaction mixtures, gas chromatographic analysis was performed with coinjection of authentic samples of known concentration and mass spectrometric analysis (at Organic Research Center in Chem. Dept., Sogang Univ.) was followed whenever necessary.

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The Isoparametricity and Non-Interaction Phenomena in the Reactions of Benzyl Benzenesulfonates with Anilines

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The nucleophilic substitution reactions of benzyl benzenesulfonates with anilines have been studied in dimethylsulfoxide-tetrahydrofuran mixtures (1 : 3 and in part 1 : 1, v/v) with varying substituents in the nucleophile (X), substrate (Y) and leaving group (Z). Total second-order interactions between variable factors provide experimental evidence for the isoparametricity phenomenon : at the isoparametric points (IPPs), $\hat{\sigma}_X$, $\hat{\sigma}_Z$ and \hat{T} (isokinetic temperature) the rate of nucleophilic displacement does not change with variation in substituents Y, i.e. $\rho_Y=0$; after passing through these IPPs, the order of reactivity for the substrate is reversed. Significant third-order interaction ($Q_{XYT}=-1.66$) provides realization of the non-interaction phenomenon: at critical values of $\hat{\sigma}_{Y(XY)}=0.08$ and $\hat{\sigma}_{X(YT)}=-0.26$ corresponding second-order interactions between temperature and substituents X (Q_{XT}) as well as substituents Y (Q_{YT}) vanish; after passing through these critical values the sign reversals for Q_{XT} and Q_{YT} are observed. The first- and second-order sensitivity coefficients as well as the IPPs were used for characterization of the transition state structure.

Introduction

Interactions between structural factors, i.e. their non-additive effects, have been of interest in the studies of the reaction mechanism and have been used for characterization of transition state (TS) structure.¹⁻⁴ In the simplest case cumu-

lative effects of substituents, *i* and *j*, on the reactivity are described by Eq. (1). The cross-interaction coefficient, ρ_{ij} , can be determined from Eqs (1-3).

$$\log k_{ij} = \log k_{(0)} + \rho_i^0 \sigma_i + \rho_j^0 \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (1)$$

$$\rho_i = \rho_i^0 + \rho_{ij} \sigma_j \quad (2)$$