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NICKEL SULFATE CATALYZED CHLORINE EXCHANGE REACTION OF BENZYL CHLORIDE WITH HYDROGEN CHLORIDE IN A NON-AQUEOUS SOLVENT

By

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Abstract

Although benzyl chloride does not undergo any chlorine exchange reaction with hydrogen chloride dissolved in cyclohexane, the presence of the calcined nickel sulfate catalyst induced the title reaction. The exchange rate was found to be closely dependent on the amounts of acid sites at $H_o \leq +3.3$ on the catalyst surface. The result obtained in the present study gives some support to the previously assumed mechanism of the benzylation reaction of benzyl chloride with aromatic hydrocarbons, where hydrogen chloride adsorbed on nickel sulfate was suggested to act as a Lewis acid.

Introduction

Among interesting catalytic activities shown by nickel sulfate heat-treated at several temperatures,[1] benzylation of alkylbenzenes with benzyl chloride[2,3] deserves some attention in view of its selectivity shown and its having an induction period at the initial phase of the reaction. As a matter of fact, the induction period observed was previously suggested to be due to the accumulation of the adsorbed hydrogen chloride on the surface of the nickel sulfate catalyst. The HCl adsorbed on the solid surface appears to be much different from that simply dissolved in a non-aqueous solvent. For example, HCl dissolved in toluene did not catalyze the Friedel-Crafts reaction, whereas it behaved as a good catalyst in the presence of inorganic solids such as metal sulfates, silica gel and alumina.[2] On the other hand, a secondary halide such as 1-phenyl ethyl chloride racemizes and undergoes a chlorine exchange reaction by HCl dissolved in a non-aqueous solvent, where both rates are identical

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indicating the formation of the same common intermediate, phenyl ethyl carbonium ion, in which the non-dissociated HCl acting as a Lewis acid forms a bichloride ion.[4]   A recent study of the chlorine exchange of benzyl chloride with the HCl dissolved in non-aqueous solution shows no evidence of the exchange under the conditions studied.[5]   It is, therefore, of interest to carry out the same reaction in the presence of the nickel sulfate catalyst.   This will shed more light on the role of the HCl in many of the $NiSO_4$ catalyzed reactions involving alkyl chlorides.   It is also rewarding to compare this exchange reaction with that studied by TANABE *et al.*[6] in a water solution, where the inorganic species concerned are all dissociated, the chlorine exchange taking place through a nucleophilic attack of chloride anion.   No Brönsted acid catalysis was observed for this reaction,[6] but certainly the Lewis acid having affinity toward the chloride anion can be a catalyst for this type of reaction.[7]

Our study on the title subject, therefore, attempts to answer some of the questions raised as to the mechanism of the nickel sulfate catalyzed reaction by establishing a relationship, if any, between the acidic property and the catalysis in the exchange reaction.   The solvent selected in this study was cyclohexane because this is not only a non-aqueous solvent, but also lacking any Friedel-Crafts type reactivity such as observed in aromatic solvents which were previously used for these reactions by others.[5]

Experimental

Reagents

Radioactive hydrogen chloride was prepared from radioactive sodium chloride as described in the next section.   Radioactive sodium chloride was prepared by adding sodium hydroxide solution to about 4.5 N hydrochloric acid containing radioactive chlorine obtained from U. S. Atomic Energy Commission which was diluted with non-radioactive hydrochloric acid and by recrystallizing it.   The radioactive chlorine is ^{36}Cl having a half-life of 4.4×10^5 years.

Benzyl chloride (Kanto Chemical K. K., reagent grade) was fractionally distilled three times to collect the portion boiling at 61–64°C at 9 mmHg and was stored in about a $2\,m\ell$ glass ampoule which was kept in a refrigerator after wrapping with aluminum foil.   Cyclohexane used as a solvent (Kanto Chemical K. K., reagent grade) was washed with concentrated sulfuric acid and then distilled three times over sodium metal to remove an aromatic impurity.   The distillation apparatus was protected from moisture with calcium chloride tubes.   The solvent was kept in a refrigerator after purification and used within 48 hours after distillation.

Nickel sulfate (Kanto Chemical K. K., reagent grade) used as a catalyst

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was prepared by heating about 1.5 g of the heptahydrate in a Hario glass ampoule of about 5 mℓ capacity and 10 mm in diameter at the specified temperature for 3 hours in an electric furnace, followed by sealing the ampoule immediately after its removal. After the ampoule cooled, the content was pulverized in a mortar to obtain 100–200 mesh samples, which were stored in an ampoule containing a desiccant, calcium chloride, wrapped with cotton wool.

Other reagents such as sodium metal, nitric acid, isopropyl alcohol, methyl alcohol, sulfuric acid, nitric acid, silver nitrate and toluene were used as received without any further purification.

Preparation of cyclohexane solution of hydrogen chloride

Fig. 1 shows an apparatus used for preparing the cyclohexane solution of hydrogen chloride. Vessel A is charged with concentrated sulfuric acid to which radioactive sodium chloride was added after freezing with liquid
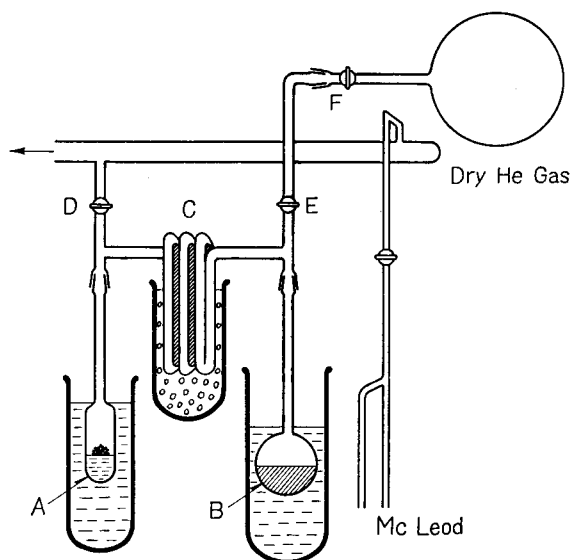

Fig. 1. Apparatus used for preparing cyclohexane solution
of HCl. Vessel A: 50 mℓ, Vessel B: 100 mℓ.

nitrogen, followed by connecting with a vacuum system. Vessel B containing cyclohexane was also connected to the vacuum line and frozen with liquid nitrogen. After reaching $10^{-5} - 10^{-6}$ mmHg, stop cocks D and E were closed and vessel A was gradually brought up to the ambient temperature. The hydrogen chloride generated in vessel A by the reaction of sodium chloride with sulfuric acid was condensed in cyclohexane in vessel B, after passing

through an acetone-dry ice cooled trap C. The vessel A was warmed with lukewarm water to complete the reaction and then stop cocks E and F were opened to introduce dry helium gas to restore an atmospheric pressure for the portion DCEAB, after which the vessel B was removed from the vacuum line.

Exchange reaction

A 500 mg of nickel sulfate was put into a round bottom flask of about 10 mℓ volume having a neck of 9 mm in diameter and 150 mm in length and the desired amount of benzyl chloride was added by a micropipette. After sealing the opening with a polyethylene film, the flask was placed in a simple dry box shown in Fig. 2. The above mentioned vessel B was rapidly connected to a ground joint G. After warming slowly to room temperature, the content of vessel B was transferred into a burette. Joint G was then connected to a balloon filled with dry helium gas. This balloon was used to give a positive pressure to the burette to force the content down into the reaction tube and at the same time to prevent hydrogen chloride gas from escaping. The dry box is kept dry by a constant passage of nitrogen gas dried by passing through a silica gel tower. Opening stop cocks H and I, 5.00 mℓ of the cyclohexane solution of HCl in a burette was placed in a reaction tube and the tube was covered with polyethylene film at its opening and removed

Fig. 2. Dry box used for filling reaction tube.

from dry box. After freezing the content with dry ice, the reaction tube was sealed. The tubes thus prepared were stored in dry ice before use. The amount of benzyl chloride was measured by volume using a micropipette, whereas the amount of hydrogen chloride was determined by the Volhard method using 5.00 mℓ of the same cyclohexane solution as used in the reaction taken in a separate ampoule, which was rinsed out 3 times with water to collect the content.

A bundle of 4 or 5 reaction tubes prepared as above was fastened to an electrically driven vibrator (Kyoto Denshi Kogyo K. K., vibro mixer VM–62), placed in a constant temperature bath held within $\pm 0.2°C$. About 1 minute was given for the tubes to reach thermal equilibrium and then vibration was started, the time of the start being taken as zero reaction time. After certain
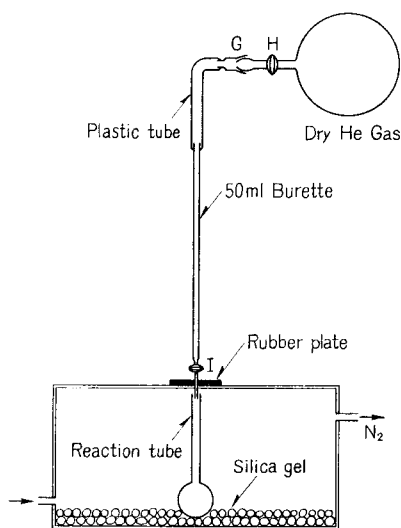
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time intervals, the reaction tube was removed from the bath and the reaction was quenched by cooling in dry ice-acetone bath. The tube was kept in a dry ice box until the following operation.

Separation of reaction product

The reaction tube kept in a dry ice box was opened and filled with de-ionized water, and then allowed to stand at room temperature until the product thawed. The content is separated from the catalyst and transferred into a centrifugal tube of 30 mℓ volume which originally had about 10 mℓ water and about 5 mℓ cyclohexane. After shaking the centrifugal tube for 1 minute, they were centrifuged for 3 minutes at the rate of 500 revolutions per minute. The cyclohexane layer was removed by a capillary tube and rinsed again by adding pure water. After repetition of this operation 5 times, the cyclohexane solution was ascertained not to contain a chloride ion by checking the washings with silver nitrate.

Measurement of radioactivity

The cyclohexane layer rinsed as above was mixed with a small amount of isopropyl alcohol to which sodium metal dispersed in toluene was added and the mixture was allowed to stand for 5–10 minutes. After the excess of sodium metal was removed by adding methyl alcohol, about 10 mℓ of pure
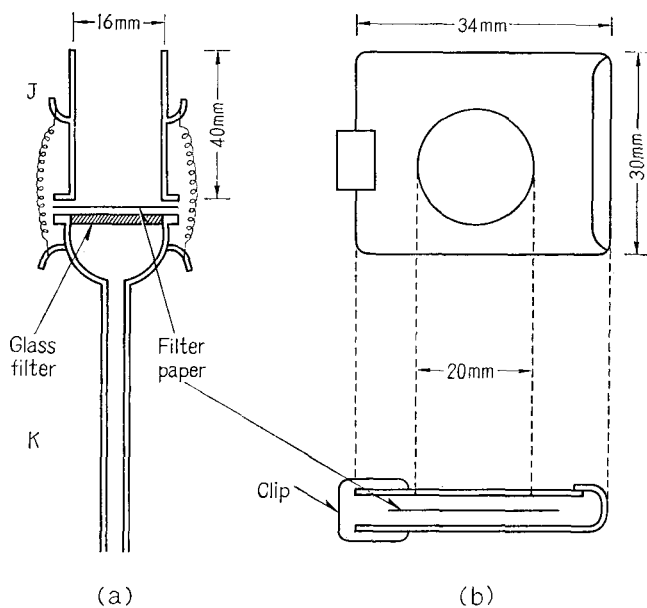

(a)   (b)

Fig. 3. Glass filter and metal holder used for preparing Ag^{36}Cl.

water was added and the mixture was neutralyzed with nitric acid using phenolphthalein as an indicator.   The water layer was filtered over a Number 5c filter paper after removing an upper cyclohexane layer with a capilliary tube.   The filtrate was mixed with excess of silver nitrate solution to give silver chloride precipitation.   This radioactive silver chloride is filtered using the filter shown in Fig. 3(a).   The filter paper used has been dried at 100–110°C to constant weight after placing on a metal holder shown in Fig. 3(b). The silver chloride filtered was rinsed with two portions of about 10 mℓ of methyl alcohol.   The filter paper was again placed on a metal holder shown in Fig. 3b and was dried until constant weight at 100–110°C after placing in a dish covered with aluminum foil.   The error in measuring the weight is ±0.1 mg.   The drying time was less than 30 minutes to prevent a thermal decomposition of silver chloride.   After reaching the constant weight, the silver chloride together with the filter paper was removed from the metal plate and placed on a stainless steel plate of 25 mm in diameter and 8 mm in depth, which was placed 5 mm off a mica window of a G–M counter (Nippon Musen K. K., Aloka Radiation Counter Model 1001) to measure the radioactivity.   The samples were always positioned on the same geometrical position against the mica window of the counter.   The measurement of radioactivity was carried out for 10 minutes to give an average value per minute, the unit being counts/minute, mg.

The self-absorption of radioactivity of ^{36}Cl is negligible if the weight of silver chloride Ag^{36}Cl is within 26 mg.[8]   This means simply that the observed radioactivity is proportional to the weight of the precipitate.   Thus, the weight of silver chloride for the radioactivity measurement was kept within the 1–20 mg range.

Specific radioactivity after infinite time

As described later, this reaction takes a very long time until reaching the exchange equilibrium; hence, an experimental determination of the radioactivity at its exchange equilibrium is difficult.   Therefore, a random distribution at the exchange equilibrium was assumed to justify the following procedure.

The same hydrochloric acid cyclohexane solution as used in the exchange reaction, 5.00 mℓ, was taken in a glass ampoule and sealed, which was opened by the procedure described in the paragraph "Separation of the Product" and the content was rinsed out three times.   After rinsing, the water layer is transferred into an Erlenmeyer flask to which hydrochloric acid of the same equivalent amount as the benzyl chloride used for the reaction was added and allowed to stand for 10 minutes after shaking.   Silver nitrate was added to precipitate silver chloride and the radioactivity was measured which gave the specific

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radioactivity after an infinite time.

Calculation of Exchange Rate

The chlorine exchange rate R of benzyl chloride with hydrogen chloride was calculated according to the following equation which is applicable to both cases in the presence and absence of a heterogeneous catalyst[9].

$$-Rt = \frac{a \times b}{a+b} \ln(1-F),\qquad(1)$$

where a and b are the molar concentration of benzyl chloride and hydrogen chloride respectively, t the reaction time and F the exchange fraction which is determined by observing the specific radioactivity of the chloride. In the present case, F is expressed as x/x_∞, where x and x_∞ are the ratios of radioactive chlorine atoms to the total chlorine atoms of benzyl chloride at t and at infinite time t_∞ respectively.

Results and Discussion

The exchange reaction in the absence of $NiSO_4$ catalyst was carried out at 62.5°C for 24 hours, but no appreciable exchange was found. In contrast to the case, the nickel sulfate catalyst catalyzed the chlorine exchange. The experiment using 500 mg of the nickel sulfate calcined at 350°C gave a significant exchange reaction, which is shown in Table 1.

TABLE 1.   Chlorine Exchange between Benzyl Chloride and Hydrogen
Chloride in the Presence of $NiSO_4$ Catalyst.

Reaction Temperature: 62.5 ± 0.2°C,
Amount of $C_6H_5CH_2Cl$: 0.335 mmol,
Amount of HCl: 0.0018 mmol,
Catalyst: 500 mg $NiSO_4$ calcined at 350°C,
Volume of Reaction Mixture: 5.20 mℓ at room temperature

Reaction Time (hr)	Radioactivity of AgCl derived from $C_6H_5CH_2Cl$ (cpm)	Wt. of AgCl (mg)	Specific Radioactivity x (cpm/mg)	% Exchange $F \times 100$ (%)	$-\ln(1-F)$
6	959	19.8	48.4	57.8	0.863
12	1357	24.2	56.1	66.9	1.104
18	1276	18.2	70.1	83.7	1.812
∞	(503)	6.0	83.8	100.0	—

R (exchange rate) $= 5.90 \times 10^{-8}$ mol. sec^{-1}.
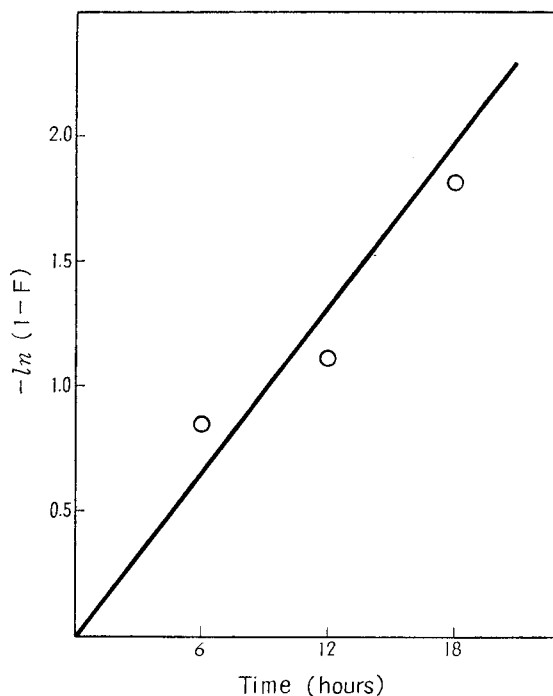
Fig. 4. Change of $-\ln(1-F)$ with time

TABLE 2. Dependence of Exchange Rate, Surface Area and Acidic Property on Temperature of Heat-Treatment of $NiSO_4 \cdot 7 H_2O$.

Reaction Temp.: $63.0 \pm 0.2°C$, Amount of $C_6H_5CH_2Cl$: 0.170 mmol, Amount of HCl: 0.00625 mmol, Catalyst: 500 mg $NiSO_4 \cdot x H_2O$ Volume of Reaction Mixture: 5.10 mℓ at room temperature

Temp. of Heat-Treatment °C	Exchange Rate $R \times 10^7$ (moℓ. sec^{-1})	Half-time of Exchange (hr.)	Amount of Acid Sites* (m moℓ/g)			Surface Area * (m²/g)
			$H_0 \leqq +4.0$	$H_0 \leqq +3.3$	$H_0 \leqq -3.0$	
150	0.745	15.4	0.027	0.023	0	6.7
250	1.65	7.0	0.095	0.084	0.029	18.2
300	3.62	3.3	—	—	—	—
325	—	—	0.14	0.12	0.063	13.4
350	3.57	3.2	0.13	0.11	0.056	12.2
375	—	—	0.12	0.11	0.055	11.2
400	—	—	0.088	0.078	0.030	10.4
464	1.19	9.7	0.067	0.043	0	8.9

*) These data were cited from ref. 10.

If the chlorine exchange reaction is taking place according to Eq. (1), a linear relationship should be obtained between the reaction time and $-\ln(1-F)$. As shown in Fig. 4, we have observed the relationship. From the inclination of the straight line, the exchange rate R was calculated to be 5.90×10^{-8} mol. sec^{-1}, using Eq. (1).

The exchange rates with various nickel sulfate catalysts calcined at different temperatures are shown in the second column of Table 2. In the third column are shown half-times of the exchange obtained at $-\ln(1-F) = -\ln 1/2$. The amount of acid sites at several acid strength H_0 ranges and surface area of the catalysts are also given in the Table.

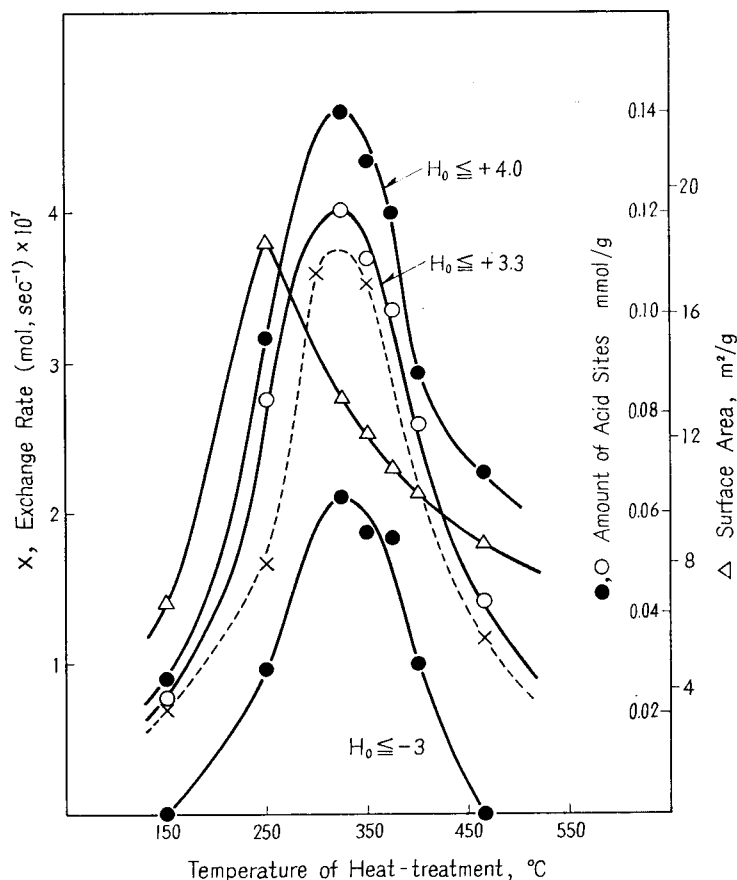In Fig. 5, the exchange rate, the amount of acid sites at $H_0 \leq +3.3$ and

Fig. 5. Relation of Exchange Rate to Acidic Property and Surface Area of $NiSO_4 \cdot x H_2O$.

at $H_0 \leqq -3.0$ and the surface area were plotted against the temperature of heat-treatment of nickel sulfate catalyst. The figure shows that the exchange rate does not depend on the surface area of the catalyst, but is very dependent on the amount of acid sites. Both of the exchange rate and the amount of acid sites increase with increasing the temperature of heat-treatment, attain a maximum value at 325°C and then decrease at higher temperatures. As seen in the figure, the nickel sulfates heat-treated at 150 and 464°C which have the acid sites at $H_0 \leqq +3.3$, but have no acid sites at $H_0 \leqq -3$ catalyze the exchange reaction. Therefore, not only the acid sites at $H_0 \leqq -3$, but also the acid sites at $-3 < H_0 \leqq +3.3$ are catalytically active. However, the exchange rate has no good parallelism with the amount of acid sites at $H_0 \leqq +4.0$ or $H_0 \leqq +4.8$.[1] It was thus concluded that the exchange reaction is catalyzed by the acid sites of $H_0 \leqq +3.3$.

As indicated in earlier part of this section, the chlorine exchange between benzyl chloride and hydrogen chloride does not take place in a non-polar solvent such as cyclohexane in the absence of a solid acid catalyst, but does occur significantly in the presence of a nickel sulfate catalyst. This result is in contrast to the result of the chlorine exchange reaction of 1-phenyl ethyl chloride in a non-aqueous solution reported by POCKER *et al.*[4]

$$RCl + H^{36}Cl \rightleftharpoons R^+ (ClH^{36}Cl)^- ,$$
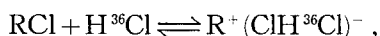
where such intermediate as bichloride ion is assumed to be present. This is due to the contention that the phenyl ethyl cation is a much more stable entity in comparison to the benzyl cation.

In the present case, the activation of both substrates may be considered to take place as shown below without giving rise to the formation of an unstable benzyl cation.
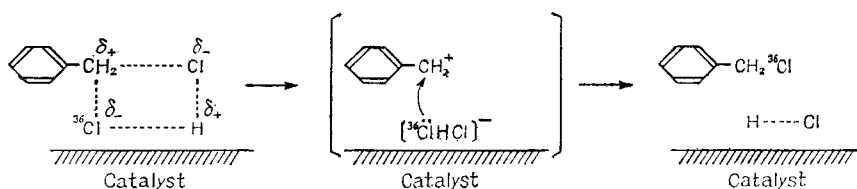
There is ample evidence supporting a Lewis acid catalyzed reaction of benzyl choride in its substitution reaction, such as a silver ion catalyzed hydrolysis.[7] The observation that the rate of the chlorine exchange reaction is proportional to the number of acid sites at $H_0 \leqq +3.3$ on the solid nickel sulfate surface seems to indicate that the adsorption of hydrogen chloride onto the catalyst surface is dependent on the number of the acid sites.

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The presented model seems to fit in the HCl–NiSO$_4$ catalyzed benzylation of alkylbenzenes[3] in that the partially dissociatively adsorbed hydrogen chloride is acting as a Lewis acid in developing a partial positive charge on the benzyl carbon where the nucleophilic attack of alkylbenzene occurs simultaneously. However, the fact that the benzylation rate was dependent on the apparent surface area, whereas the chlorine exchange was not, but dependent on the number of acid sites needs some explanation. It may mean that the amount of aromatic hydrocarbons adsorbed in the benzylation reaction is proportional to the surface area of the nickel sulfate catalyst covered with hydrogen chloride gas which may not be as strongly held as that on the relatively strong acid sites at $H_0 \leq +3.3$ required for the exchange reaction. It will be of much interest if the benzylation reaction is carried out simultaneously with the exchange reaction, using an aromatic hydrocarbon as a reactant and a solvent in place of cyclohexane.

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