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## NOTE

### NICKEL SULFATE CATALYZED REACTION OF BENZYL CHLORIDE WITH TOLUENE

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We have hitherto presented several cases of acid catalyzed reaction over solid metal sulfates in which the substrate base, either carbon, nitrogen or oxygen compound, coordinated with the acid sites on the surface.<sup>1)</sup> This catalyst system is now extended to other *n*-base, alkyl halide. The reaction investigated in this paper is a Friedel-Crafts type benzylation of an aromatic hydrocarbon with benzyl chloride in the presence of the nickel sulfate calcined at various temperatures.

The nickel sulfate catalyst was prepared in the usual manner by heating in air of a guaranteed reagent grade heptahydrate at 150–450°, and stored in a sealed ampoule until use. Benzyl chloride was a fractionally distilled product, whereas toluene and other aromatic compounds used were guaranteed reagents. The rate of the benzylation reaction was determined by the amount of HCl evolved. In a 500 ml three-necked flask with a stirring rod, a nitrogen inlet and an efficient spiral condenser, fitted with a HCl gas outlet connected to a titration assembly, was placed 50 ml of 1 M. benzyl chloride in toluene and 1.2 g of accurately weighed nickel sulfate. The evolved HCl gas was delivered by N<sub>2</sub> gas into a vessel containing 50 ml water, equipped with a pH electrode and a syringe burette (SBU 1 type), connected to a SBR 2 Titrigraph with a type TTT 1c Automatic Titrator of Radiometer, Copenhagen, Denmark. As about 5 ml of an alkali solution (11.37 N NaOH) is needed for titration, an original syringe was replaced by one with 10 ml capacity. The pH stat recording was done at the end-point pH 3.5, with a chart speed, 1.25 mm/min.; pen speed, 4%/min. The assembled burette system was calibrated using 1 N NaOH and 1 N H<sub>2</sub>SO<sub>4</sub> solution. The 100% range of a micrometer revolution was found to correspond to 5.07 ml in volume. The reaction was started by immersing the reaction vessel in an oil bath (121.6±0.2°C) with mechanical stirring and introduction of N<sub>2</sub> to sweep the HCl gas into the titrator. Time zero was read from the recorded titration curve as a point at which the titrator initiated its action, usually with a short period of induction (~5 min.). A typical pH stat

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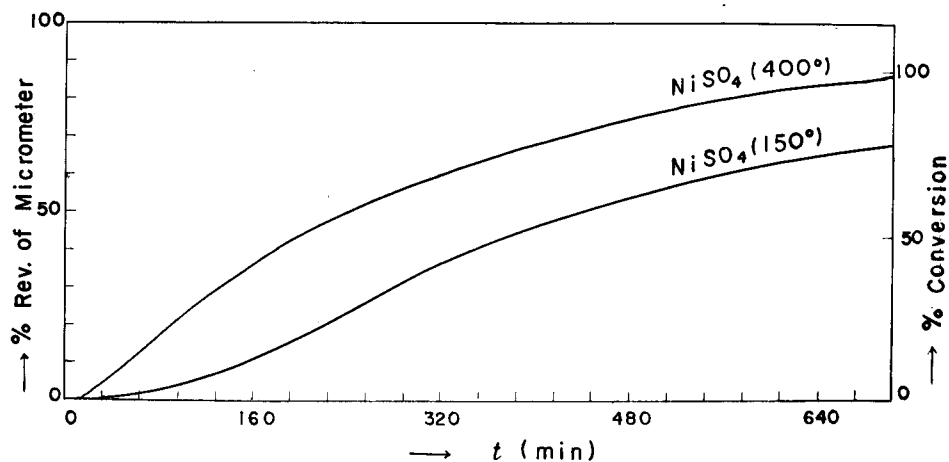


Fig. 1. Consumption of NaOH vs. time recorded by a pH stat, SBR 2c Titrigraph.

Reaction Condition: Benzyl Chloride, 1 M 50 ml toluene solution  
Catalyst, 1.2 g; Bath Temp.  $121.6 \pm 0.2^\circ\text{C}$ .

record is reproduced in Fig. 1.

In every case an initial part of HCl evolution was linear with time, but the over-all reaction followed a first order kinetics with respect to benzyl chloride concentration, as shown in Fig. 2, up to well over 50% completion. Table 1 summarizes the rate constants obtained, together with the pertinent data taken from our previous study<sup>1b)</sup>. Evidently, the rates are not directly related to the acidities of the catalyst (Fig. 3), but rather proportional to the available surface of the catalyst (Fig. 4). Plot of the BET area ( $\text{m}^2/\text{g}$ ) vs. the rate constant  $k_1$ , as shown

TABLE 1. Benzylation Rates of Toluene by Benzyl Chloride over NiSO<sub>4</sub> Catalysts, Bath Temperature  $121.6 \pm 0.2^\circ\text{C}$ .

NiSO <sub>4</sub> Temp. of Heat Treatment ( $^\circ\text{C}$ )	Acidities* <sup>1)</sup> $pK_a = 4.8, \text{mmole/g}$	Surface* <sup>2)</sup> Area $\text{m}^2/\text{g}$	$k_1 \times 10^3$ $\text{min}^{-1}\text{g}^{-1}$	Initial rate $\times 10^3$ $\text{mol } \ell^{-1}\text{min}^{-1}\text{g}^{-1}$
150	0.031	6.7	3.48	2.39
200	0.072	15.0	8.94	5.35
250	0.091	18.2	10.9	8.79
350	0.115	12.2	4.96	4.05
400	0.086	10.4	3.16	2.84
450	0.069	9.2	5.27	4.13

\* Taken from ref. 1b). Those for 200° and 450° were read from the data.

Note

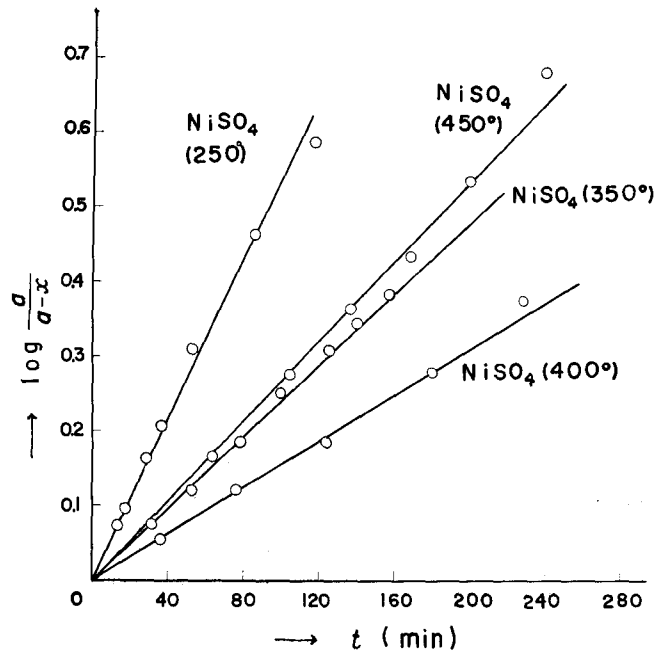


Fig. 2 a. Typical plot of  $\log a/(a-x)$  vs. time.

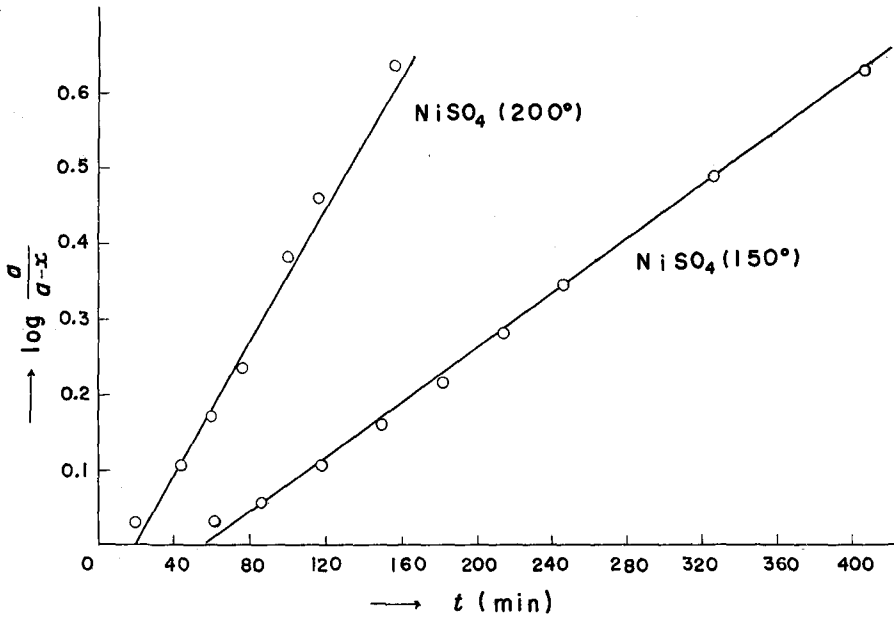


Fig. 2 b. Typical plot of  $\log a/(a-x)$  vs. time.

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in Fig. 4, gives this rather unexpected result. Although it is not known whether the BET surface area reflects the real significance in this reaction condition, the apparent correlation indicates an interesting aspect of this heterogeneous reaction.

The benzylation by a homogeneous LEWIS catalysis is known to proceed in a polar solvent: by the following rate expression<sup>2),3)</sup>,

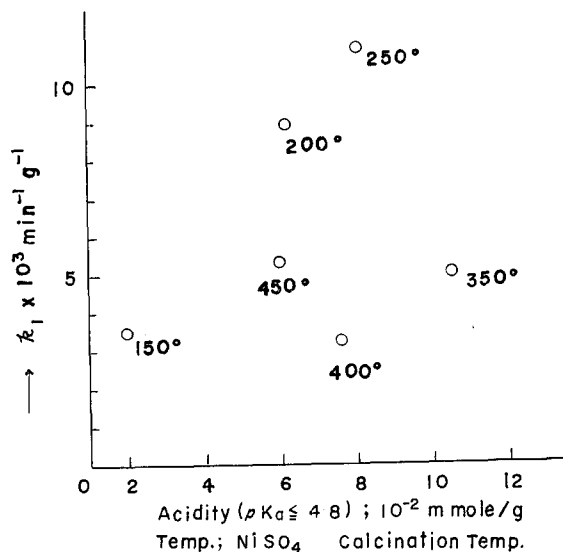


Fig. 3. Lack of correlation of the rate with the surface acidity of NiSO<sub>4</sub>.

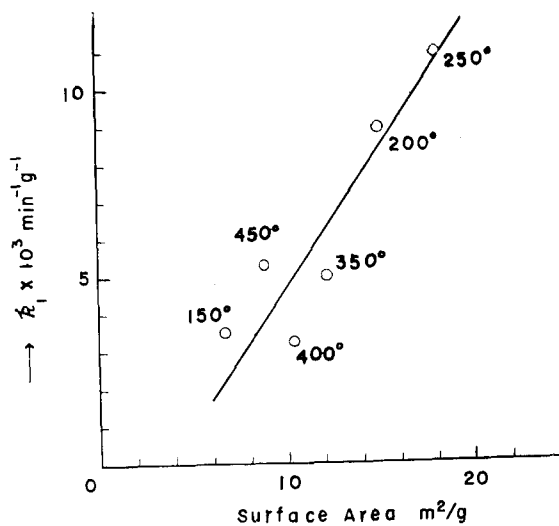
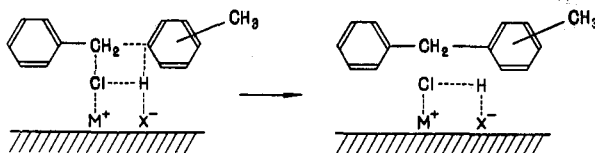


Fig. 4. Correlation of the rate with the BET area of NiSO<sub>4</sub>.

Note

$$\frac{d[\text{HCl}]}{dt} = k_3 [\text{ArH}] [\text{AlCl}_3 \cdot \text{Nitrobenzene}] [\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]$$

containing a term for the aromatic hydrocarbon to be benzylated, which has been interpreted by BROWN<sup>2)</sup> *et al* as a nucleophilic displacement type rather than a free benzyl cation as an active species. The outcome of this mechanism is dependence of reactivity on the basicity of the hydrocarbon used, which is exactly what is found. OLAH's data<sup>3)</sup> show  $k_{\text{toluene}}/k_{\text{benzene}} = 3.20$ ;  $k_{\text{bromobenzene}}/k_{\text{benzene}} = 0.18$ , hence,  $k_{\text{Br}}/k_{\text{toluene}} = 0.056$ . Our observation points to the similar type of the reactivity. For example, an attempt to benzylate bromobenzene, at the condition that was good for toluene by nickel sulfate, failed, and the reaction with benzene was much slower. Since the acidic sites of nickel sulfates are not directly controlling the reaction but the rates are linearly related to the available surface, the role of the solid surface may be important by providing a polar medium for this reaction. The generation of benzyl cation in a homogeneous polar solvent has been shown by its kinetic isotope effect  $k_{35}/k_{37}$ , but this cationic nature is decreased by increasing nucleophilicity resulting in acceleration of the over-all rate<sup>4)</sup> Although any mechanistic discussion is obviously premature at the present state of scant data, it is tempting to postulate that the anionic sites of nickel sulfate may be just as important as the cationic sites, for example:



A bipolar nature of the solid acid catalyst is not new.<sup>5)</sup> SCHWAB<sup>6)</sup>, particularly, pointed out the resemblance of the function to an elimination of HCl from alkyl chloride. The postulation is compatible with the kinetics,

$$\frac{d[\text{HCl}]}{dt} = k_2 [\text{C}_6\text{H}_5\text{CH}_2\text{Cl}] [\text{Cat. Surface}]$$

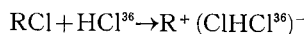
in which the term for [toluene] does not appear since it is present in excess.

An alternative attractive mechanism would be an HCl catalyzed path on the catalyst surface. There are repeated demonstration of HCl assisted ionization of alkyl chloride through its electrophilic hydrogen bonding. For example, the rates of racemization, and chlorine isotope exchange reaction of 1-phenyl ethyl chloride contain a bimolecular kinetic term; first order in substrate as well as in HCl<sup>7)</sup>.

$$V = k_1 [\text{RCl}] + k_2 [\text{RCl}] [\text{HCl}]$$

Moreover in this particular instance, a relation of  $k_{2\text{rac.}} = k_{2\text{exchange}}$  indicates a common process by aiding heterolysis of halide by HCl through bichloride ion

formation.



This bichloride ion is not only a kinetic entity, but such salt as  $(\text{Me})_4\text{N}^+\text{Cl}_2^-\text{H}$  has been actually isolated<sup>9)</sup>. HART and CASSIS<sup>9)</sup> observed an autocatalytic action of HCl in the absence of added catalyst for tritylation of phenol in a non-polar solvent where the kinetic rate plot was a typical S-shaped one. As mentioned briefly we have also observed some induction, the extent of which has seemed to be inversely proportional to the acidity of the catalyst. If we take a period till 1% conversion as an induction period  $T_{1\%}$ ,  $1/T_{1\%}$  appears related to the acidity. The values of  $1/T_{1\%} \times 10^2$  for the  $\text{NiSO}_4$  of 150, 200, 250, 350, 400 and 450°C are 4.2, 13, 19, 17, 7.0 and 10, respectively. Therefore, the function of the intrinsic acidic sites on the catalyst may be only in initiating the reaction. Then the initially formed HCl on the catalyst remains adsorbed on the surface; this adsorbed HCl, in turn, acts as a true catalyst. This model is attractive in explaining the induction period and apparent lack of correlation of the rate with the acidities of the  $\text{NiSO}_4$  catalyst. The amount of the HCl retained on the activated catalyst should be, of course, in proportion to the available surface area, which is just as observed in Fig. 4. In a sense, the HCl has exerted a levelling effect for the catalyst. Choice of these mechanisms, and whether a  $\pi$ - or  $\sigma$ - complex is involved in this benzylation are not possible at this stage awaiting a further investigation.

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