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Charge Transfer Effects in Friedel-Crafts Reactions on Germanium

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The reaction of α-chlorotoluene and benzene to yield diphenyl methane, catalyzed by germanium has been studied as a function of the bulk electrical properties of the germanium catalyst. The activation energy for the reaction is a linear function of the Fermi energy as determined from bulk measurements of the resistivity. The p-type catalysts were the most active as would be expected from the Lewis acid nature of known catalysts for Friedel-Crafts reactions.

INTRODUCTION

Attempts to relate the catalytic activity of semiconductor surfaces with their solid-state electrical properties are well-known, but the predictions of the so-called charge-transfer theories of catalysis (*1–5*) even in their most elegant forms (*1*, *6*) have never been in essentially quantitative agreement with experimental results with perhaps the possible exception of the photoinduced electrochemical reactions on zinc oxide (*7*). One obvious reason is that much of the experimental work has been carried out on oxides, whereas until recently (*8*) the physical theory employed has been more applicable to elemental semiconductors of Group IV. On the other hand, even studies on elemental semiconductors (*9–11*) have not revealed the relatively simple predictions of the theory. One or more of three major experimental problems may have obscured the results of most investigators:

1. Semiconductor surfaces must be prepared under ultraclean conditions to avoid background contamination which can dominate the surface electrical properties.
2. In studies involving the effects of doping, the temperature of the semiconductor must be kept below the level where intrinsic conduction dominates the system.
3. Many reaction systems react irreversibly with the fresh semiconductor surface to produce a surface electrical state which is unaffected by the bulk properties of the semiconductor and can be related primarily to the temperature history of the catalyst after contacting the reactant (*11*).

It is the purpose of this paper to report some results on the reaction of benzene and α-chlorotoluene catalyzed by germanium surfaces which indicate that this system, and by implication the Friedel-Crafts reactions in general, may overcome these difficulties and thus provide an opportunity to test in a rigorous fashion some of the predictions of the charge-transfer theories. That germanium is an active catalyst for Friedel-Crafts reactions and sensitive to the bulk electrical properties of the solid was first demonstrated by Watson (*12*).

RESULTS

The experiments reported here were carried out in the liquid phase under a flowing blanket of gettered nitrogen, an approach that has been shown to reduce the oxygen content of aqueous systems below that required to produce a fraction of a monolayer on a few square centimeters of germanium surface (*13*). Several hundred cm^2 of fresh germanium surface were produced by *in situ* cleavage through vigorous stirring (*14*) of a reaction mixture composed of benzene, α-chlorotoluene, and large chunks of uncleaved germanium. During cleavage, the primary germanium particles were suspended in the moving fluid. Cleavage took place as these particles collided with the walls of the vessel, the thermowell, the sparger, etc. Thus the size reduction was accomplished without the application of the large forces usually encountered in heavy milling and standard grinding operations. This is important because such forces would most assuredly lead to large densities of surface dislocations. While no conclusive evidence can be given for the absence of surface dislocations in this work, it is believed that the cleavage method used would tend to minimize their production. The rate of reaction was measured by bubbling the effluent nitrogen through a standard NaOH solution for a timed interval and then titrating the unreacted NaOH. The analysis was sensitive enough to permit a complete characterization of a single solid sample without depleting the reactants appreciably or achieving large concentrations of product, diphenylmethane. Temperature was controlled with a thermostated water bath.

In experiments where the reactant concentrations were changed during a run a calibrated dropping funnel (also degassed and blanketed with gettered nitrogen) was used to add amounts of benzene successively to a reaction mixture originally rich in α-chlorotoluene. It was observed that after a certain initial period (1–4 hr) that the reaction rate was constant with time even with vigorous stirring. All data reported are for reaction times after the constant rate had been reached. This period of constant rate presumably indicated that most of the germanium has been pulverized into small enough particles that very little further cleavage to produce newly exposed surfaces was occurring. Surface areas were estimated crudely from microscopic particle size measurements and were found to be about 100 cm^2/g. The particles produced by this cleavage were angular polyhedra and probably expose mostly (111) germanium surfaces since this is the plane of easy cleavage.

The germanium was obtained from Eagle-Picher Corporation and approximately characterized by the manufacturer. Hole concentrations are calculated from the conductivities reported by Eagle-Picher. Benzene (Baker) and α-chlorotoluene (Matheson) were reagent grade.

A series of rate measurements were made on several samples of *n*-type (Sb doped) and *p*-type (Ga doped) as well as an intrinsic sample between room temperature and about 70°C. All of the samples gave linear Arrhenius lines with activation energies between 2 and 8 kcal/mole. Calculation of the rate of diffusion to the catalyst particles (*15*) indicated that diffusion is several orders of magnitude greater than the measured rates, and variations of the stirring rate had no effect on the observed rate of reaction as long as the stirring was vigorous enough to keep the catalyst particles suspended. Figure 1 shows how the activation energy varies as a function of the number of positive holes in the bulk of the germanium. This linear relationship with the log of the hole concentration means that the activation energy is linearly related to the position of the Fermi energy of the solid, a very simple correlation indeed compared to those often observed. The lowest activation energies and consequently the highest reactivities were found for the *p*-type catalysts as would be expected since Lewis acids are known to catalyze Friedel-Crafts reactions.

The effect of reactant composition is seen in Fig. 2 where the log of the rate is

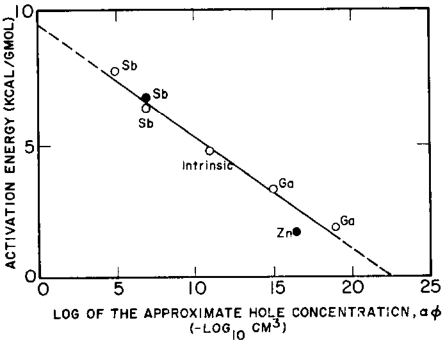


FIG. 1. Correlation of activation energy with bulk electrical properties; ○, this work; ●, Blossey (*15*).

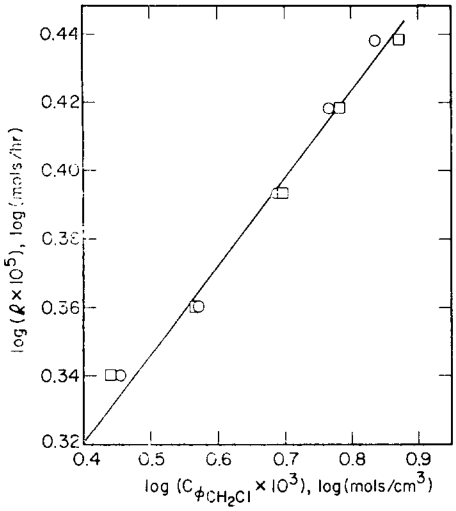


Fig. 2. Effect of concentration on overall rate. Reaction order = 0.25; ⊙, *n*-type; ⊡, *p*-type.

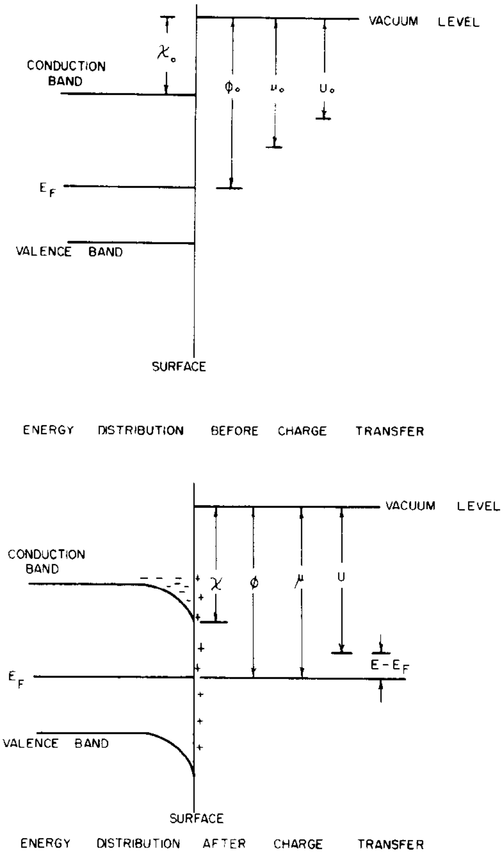
plotted against the log of the α-chlorotoluene concentration for both an *n*-type and a *p*-type sample at room temperature. The plot gives an apparent order of reaction of 0.25. This low apparent order is suggestive of strong chemisorption of the reacting species.

Discussion

The correlation between the activation energy and Fermi energy is consistent with a very simple view of charge-transfer catalysis. Following the approach of Volkenshtein (*1*) a strongly bound chemisorbed species can exist on the surface as an un-ionized or an ionized form. The thermodynamic driving force for charge exchange is the difference between the chemical potential of electrons in the chemisorbed molecules and the chemical potential of electrons in the solid. The latter is just the work function.

On a semiconductor surface the adsorbed molecule would result in an "impurity state" at the surface since any interruption in the periodicity of the lattice results in such a localized state. In Fig. 3, the energetics of this case is shown for the flat-band condition of a semiconductor, i.e., the case for which there is no bending of the energy bands near the surface prior to charge exchange between the surface and the adsorbed molecule. The work function is given by ϕ; the energy of the impurity state is E; the chemical potential of electrons in the admolecules is μ, and the electron affinity is χ. Subscript 0 indicates the value of these parameters after adsorption but before charge transfer. Zero energy for all quantities is taken at the vacuum level. For the case shown in Fig. 3, there is a driving force for transfer of electrons from the adsorbed molecules to the surface of ϕ_0–μ_0. Charge transfer will, therefore, continue until $\phi = \mu$. This will cause bending of the bands and a space charge layer which extends into the semiconductor surface. The population probability of the impurity state will be given by Fermi statistics

$$f = \frac{1}{1 + \exp\dfrac{E - E_f}{kT}}. \qquad (1)$$



ENERGY DISTRIBUTION BEFORE CHARGE TRANSFER

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Fig. 3. Energetics of charge transfer.

The partitioning energy in the Fermi distribution function is just the difference between the energy of the surface state and the chemical potential in that surface state, i.e., $E - E_f = \mu - U$. It should be noted that in the general case all of the energy parameters change with charge exchange. The simplifying assumption implied by Volkenshtein's treatment (*1*) is that there is no perturbation from U_0 as charge transfer takes place. This means that U is independent of bulk doping while ϕ and μ, and hence the partitioning energy, $E - E_f$, are directly proportional to the Fermi energy and, therefore, controllable by bulk doping of the semiconductor. If, for example, only the ionized form of an adsorbed molecule were catalytically active, then the bulk doping would regulate the catalytic activity by controlling the fraction of the adsorbed species which are ionized. The Lewis acid nature of catalysts for Friedel-Crafts reactions make it quite reasonable that the active surface species may be an ionized donor. The Fermi distribution function (Eq. 1) is related to the fraction ionized, θ_i, and the fraction unionized, θ_0:

$$\frac{\theta_0}{\theta_0 + \theta_i} = f, \tag{2}$$

which can be rearranged to give

$$\frac{\theta_i}{\theta_0} = \exp\frac{E - E_f}{kT} = \exp\frac{-U + \phi}{kT}. \tag{3}$$

The fact that the apparent rate order for n-type is identical to that for p-type suggests that the total amount adsorbed is independent of bulk doping, and thus the rate should be proportional to θ_i/θ_0. From this it follows that the apparent activation energy for the overall reaction is

$$E_a = E_c + U - \phi. \tag{4}$$

Where E_c is the apparent activation energy for the adsorption and reaction steps. In the Volkenshtein approximation where U is always fixed at U_0, the activation energy is directly proportional to ϕ with a negative slope of unity. The results in Fig. 1 are proportional to ϕ, but the slope is —0.6 instead of the predicted minus one. An important assumption implied by the Volkenshtein model is that there are no charge-transfer induced perturbations on the various energy parameters. Attempts to account only for the electrostatic perturbations induced by charge transfer (*16*) have shown that U probably does not remain constant at U_0 but tends to "track" with changes in the Fermi energy, so that the Volkenshtein estimate is surely an upper limit to the magnitude of the change that bulk doping can introduce.

The smaller slope of Fig. 1 is interpreted as evidence for charge-transfer induced perturbations. If so, then the maximum change in E_a in going from decidedly n-type to decidedly p-type germanium should be calculable from the slope of Fig. 1 and the band gap of germanium. Using 15 kcal/mole for the band gap this gives a maximum ΔE_a of 9 kcal/mole. The actual ΔE_a depicted in Fig. 1 is about 6 kcal/mole. This is acceptable agreement since no degenerate n-type and/or p-type samples were tested so the full band gap was not traversed.

It cannot be said for certain from this work whether this system is in fact dominated by charge-transfer effects, and certainly the consistency of these measurements with the oversimplified Volkenshtein model is not, itself, adequate evidence for accepting the model. Indeed experiments on cleaved surfaces of germanium in vacuum show that the work function of the clean surface (*17*) is not proportional to the work function, nevertheless, this simple relationship between the reactivity and the bulk properties of the germanium make it seem plausible that Friedel-Crafts catalysis by germanium does not suffer from some of the difficulties which have obscured previous attempts to investigate quantitatively the predictions of the charge-transfer theory, but detailed evaluation of the more complete forms of the theory cannot be expected until the electrical properties of the catalytically active surface are investigated.

To this end work on this system is continuing in this laboratory in an ultrahigh-vacuum system where the germanium surfaces can be prepared by ion bombardment and annealing, and characterized by low-energy electron diffraction and atomic helium scattering (*18*). Surface electrical properties are being measured as a function of the adsorption of the reactants and products. It is hoped that the results of this work will produce a more definitive statement about the quantitative details of charge-transfer controlled catalysis at semiconductor surfaces.

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