

and the steric effect to be the major factor. Phenacyl chloride reacts with iodide ion in acetone 9,000 times more rapidly than does *n*-butyl chloride. If methyl groups are successively substituted into the phenacyl side chain, the resulting secondary and tertiary halides should still be extremely reactive if inductive effects are the deciding factor, but the reactivity should decrease many fold for each methyl group substituted if steric effects are of major importance. The argument for the first statement, assuming inductive effects to be of major importance, is that the increase in electron density at the reacting carbon atom due to the electron releasing ability of the methyl groups must be insignificant compared to the decrease in electron density due to the adjacent carbonyl group. Otherwise a carbonyl group adjacent to a  $-\text{CH}_2\text{Cl}$  group would not increase the  $\text{S}_{\text{N}}2$  reactivity nine thousand-fold whereas a methyl group in the same position decreases the reactivity ten to twenty-fold at most (methyl *versus* ethyl halides in various  $\text{S}_{\text{N}}2$  reactions).<sup>2</sup> Accordingly, the substitution of methyl groups into the phenacyl side chain should not change the electron density at the reacting carbon atom appreciably, and the reactivity should show little change as one progresses from the primary to the secondary to the tertiary keto halides. On the other hand, if steric effects are deciding, the secondary halide should react much more slowly than the primary halide (as happens when one goes from *n*-butyl chloride to *sec*-butyl chloride in typical  $\text{S}_{\text{N}}2$  reactions) and the tertiary halide should be even less reactive. This is the way the reactivities of phenacyl chloride,  $\alpha$ -chloropropiophenone and  $\alpha$ -chloroisobutyrophenone

were, in fact, found to be. All of our data have been obtained at 0°, and are summarized in Table I.

The above data show that the relative reactivities of primary, secondary and tertiary chlorides in the phenacyl series are 1:0.006:0.000003. This is a more pronounced change than is encountered in the butyl chloride series, and, in view of the previous argument, appears to provide conclusive evidence that the decrease in reactivity as one goes from primary to secondary to tertiary halides is almost entirely due to a steric effect. The two thousand-fold decrease in reactivity as one goes from the secondary to the tertiary chloride is outstanding, and suggests that the keto chloride rate values illustrate the relative reactivities of primary, secondary and tertiary halides in a reaction going entirely by the  $\text{S}_{\text{N}}2$  mechanism better than the usually given butyl chloride rate values. We are now studying more carefully the reaction of *t*-butyl chloride with sodium iodide to determine if an  $\text{S}_{\text{N}}1$  mechanism contributes appreciably to its relatively high reactivity.

If inductive effects are of little importance, one wonders why phenacyl chloride is as reactive as it is. Several investigators<sup>4</sup> have suggested that an approaching nucleophilic group can form a loose bond with the carbon atom of the polarized carbonyl group in the transitional state and thus be in a sterically favorable position for the ensuing nucleophilic attack on the alpha carbon. In chloromethyl *p*-tolyl sulfone, this cannot happen unless the valence shell of the sulfur is expanded, and an unreactive halide is the result. The unreactivity of this compound provides additional evidence of the minor role played by inductive effects.

Studies are underway on solvent and temperature effects and the more accurate determination of the *k* values of the slow reactions.

(4) Priority for this suggestion apparently belongs to J. W. Baker, *J. Chem. Soc.*, 445 (1938).

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#### SOME MAGNETIC CONSEQUENCES OF CHEMISORPTION ON SUPPORTED NICKEL CATALYSTS

Sir:

Michel<sup>1</sup> has shown that nickel-silica catalysts give thermomagnetic curves as in Fig. 1(3).

We may consider such curves as being made up of a large number of steps, each step representing a nickel particle in which the Curie temperature,  $T_c$ , is related, as a first approximation, to the average number of nearest nickel neighbors,  $z$ , by the expression  $T_c/631^\circ = z/12$ , where  $631^\circ$  and 12 are, respectively, the Curie temperature ( $^\circ\text{K}$ .) and the coordination number in massive nickel.

The average quantity  $z$  is related to particle size. Thus any point  $\sigma_{T_c}$  on the thermomagnetic curve represents that fraction of total reduced nickel present in particles in excess of a determinable size.

With this information we may construct dis-

(1) A. Michel, R. Bernier and G. LeClerc, *J. chim. phys.*, **47**, 269 (1950).

TABLE I

SECOND-ORDER RATE CONSTANTS FOR ORGANIC HALIDE REACTING WITH SODIUM OR POTASSIUM IODIDES IN DRY ACETONE AT 0°<sup>a</sup>

Compound	Time for 50% reaction if solution 0.1 <i>M</i> in each reactant	<i>k</i> in liters moles <sup>-1</sup> hours <sup>-1</sup>
<i>n</i> -Butyl chloride	111 days	0.00375 <sup>b</sup>
<i>sec</i> -Butyl chloride	5 years	<0.0026 <sup>b</sup>
<i>tert</i> -Butyl chloride	6 years	<0.0002 <sup>b</sup>
Phenacyl chloride	18 min.	33.6 <sup>b</sup>
$\alpha$ -Chloropropiophenone	50 hours	0.200
$\alpha$ -Chloroisobutyrophenone	11 years	<0.0001
Chloromethyl <i>p</i> -tolyl sulfone	No measurable reaction <sup>c</sup>	

<sup>a</sup> The reaction rates were determined by the electrometric titration with silver nitrate of the unreacted iodide ion isolated from solutions originally 0.1 *M* in each reactant. That the reactions were second order was also established by paired runs 0.2 *M* in one reactant and 0.1 *M* in the other in the case of phenacyl chloride and  $\alpha$ -chloropropiophenone. <sup>b</sup> Previous values reported<sup>3</sup> for the butyl chlorides and phenacyl chloride with sodium iodide or potassium iodide in acetone are: *n*-C<sub>4</sub>H<sub>9</sub>Cl, 0.040 at 50°, 0.10 at 60°; *sec*-C<sub>4</sub>H<sub>9</sub>Cl, 0.0022 at 60°; *t*-C<sub>4</sub>H<sub>9</sub>Cl, 0.0018 at 60°; phenacyl chloride, 22 at 0°. <sup>c</sup> Several workers have previously reported  $\alpha$ -halo sulfones to be inert, but no quantitative data are available.

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 154.

(3) J. B. Conant and W. R. Kirner, *THIS JOURNAL*, **46**, 232 (1924); J. B. Conant and R. E. Hussey, *ibid.*, **47**, 476 (1925).

tribution curves showing fraction of reduced nickel *versus* particle size. These curves show that nickel-kieselguhr catalyst as reduced at, say, 360° for ten hours, possesses few nickel particles in excess of 50 Å. on a side, but many particles ranging from 10 to 50 Å. The distribution of particle sizes is altered by time and temperature of reduction, nature of support, proportion of total nickel, and so forth.

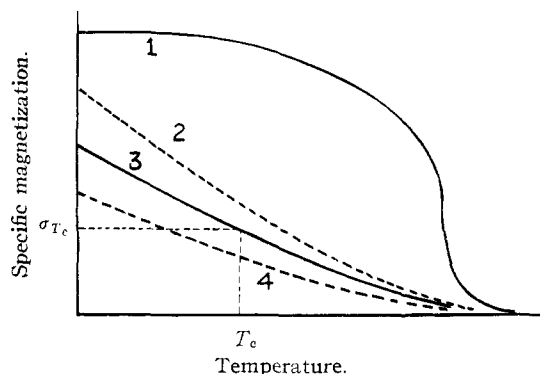


Fig. 1.—Thermomagnetic curves for (1) massive nickel, (2) reduced nickel-silica catalyst with chemisorbed nitrogen, (3) reduced nickel-silica catalyst in helium or vacuum, and (4) reduced nickel-silica catalyst with chemisorbed hydrogen.

The interesting feature of these results is that particle sizes in the 10–50 Å. range possess such a large ratio of surface to volume that chemisorbed gases are able to modify the magnetic moment of the nickel. If nickel possesses 0.6 electron hole per atom in the d-band, then a particle about 20 Å. on a side would lose all its ferromagnetism if covered with a monolayer of hydrogen molecules each of which donates one electron to the nickel particle.

We have found that adsorbed hydrogen on a nickel-silica catalyst reduces the specific magnetization of the nickel by about 20%. Ethylene has a similar effect. The temperatures at which adsorption and desorption take place are indicated with considerable precision. Nitrogen and oxygen which are chemisorbed, presumably, by abstraction of electrons from the catalyst particle, give an increase of magnetization.

Benzene, in the temperature range so far investigated, namely 100°, is almost without effect. A mixture of benzene and hydrogen at 100° gives only the decrease of magnetization due to hydrogen alone. This suggests that the hydrogenation of benzene does not necessarily involve chemisorption of the benzene and that, at least for this reaction, the Balandin geometric factor is without significance.

The method may readily be extended to other reacting systems, *in situ*, and may, in general, be expected to yield information concerning the electronic state of catalytically active systems involving ferromagnetic substances under a variety

of temperature and pressure conditions approximating those used in actual catalytic practice.

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#### FRIEDEL-CRAFTS ACYLATIONS OF PHENYLSILANES<sup>1</sup>

Sir:

We wish to report the first successful Friedel-Crafts acylation reaction carried out with a phenylsilane. In previous attempts to acylate phenylsilanes it was found that aryl-silicon bonds were easily cleaved when aluminum chloride catalyst was employed<sup>2</sup> and this cleavage has been generally attributed to the acidic nature of the catalyst. A careful consideration of the probable mechanism of the cleavage of aryl-silicon bonds has led us to the conclusion that the above-mentioned cleavage reaction depends not only on the acidity of the acylation catalyst but also on the nucleophilicity of the anion produced during the reaction, and after considerable experimentation with various acylation procedures we were able to acetylate and to benzoylate trimethylphenylsilane.

Thus, when trimethylphenylsilane, 40 g., was stirred for five hours with a mixture of 32 g. of acetyl fluoride in 150 cc. of chloroform saturated with boron trifluoride, there was obtained upon working up of the reaction mixture 12 g. of the starting material and approximately 10 g. (*ca.* 35%) of high boiling product, b.p. 80–100° (3 mm.), which gave the solid trimethylsilylacetophenone, m.p. 40–41° (*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>OSi: C, 68.72; H, 8.39. Found: C, 69.12; H, 8.25). The 2,4-dinitrophenylhydrazone was prepared in the usual way, m.p. 194–195° (*Anal.* Calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub>Si: C, 54.83; H, 5.41; N, 15.05. Found: C, 54.84; H, 4.95; N, 14.68). Similarly, the reaction of trimethylphenylsilane with benzoyl fluoride in the presence of boron trifluoride gave trimethylsilylbenzophenone, m.p. 64° (*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>OSi: C, 75.55; H, 7.13. Found: C, 75.86; H, 7.23) from which the corresponding 2,4-dinitrophenylhydrazone, m.p. 211–213° (*Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub>Si: C, 60.80; H, 5.11; N, 12.89. Found: C, 61.03, H, 5.23, N, 12.46) was prepared.

The experimental details of the above acylations, the proof of the positions of the substitution, and the experiments employing other acidic catalysts, will be described in a forthcoming publication.

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(2) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931), and references cited by R. A. Benkeser and H. R. Krysiak [*This Journal*, **76**, 599 (1954)].