that the magnitudes of the equilibria constants are determined by considerations of potential energy alone. It is clear from the observed large variations in ΔS^0 that this is not the case and that, in fact, the kinetic energy changes accompanying complex formation are not uniformly the same throughout this series. Under these conditions it becomes hopeless to attempt to correlate structure and reactivity toward complex formation in terms of potential energy considerations alone. The changes in equilibrium constant resulting from a particular substituent could stem from a whole series of effects amongst which we might list polar or inductive effects, resonance effects, steric hindrance effects, polarizability effects and solvent effects.

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NOTES

A New Preparation of Bis-cyclopentadienyl–Metal Compounds

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Three major types of reactions have been used to prepare bis-cyclopentadienyl-iron(II) and other bis-cyclopentadienyl-metal compounds: (a) the reaction of a cyclopentadienyl organometallic reagent: C_5H_5MgBr in benzene[1] or C_5H_5Na in tetrahydrofuran[2] with transitional metal halides or acetylacetonates, or C_5H_5K in liquid ammonia with a metal thiocyanate.[3] Bis-indenyl derivatives of Fe and Co also have been prepared by similar reactions[4]; (b) the reaction of cyclopentadiene vapor with a metallic iron catalyst[5a] or ferrous oxide at 350°,[5b] and (c) the reaction of cyclopentadiene vapor with a metal carbonyl.[6]

Method a depends upon the acidic character of the methylene hydrogen of cyclopentadiene which enables the formation of an organometallic derivative with the evolution of hydrogen in the reaction with Na or K, or in the case of the Grignard reagent, where cyclopentadiene reacts with C_2H_5MgBr, of ethane. The dissociation constant of the acidic hydrogen of cyclopentadiene is very small; the pK value for indene has been estimated to have a minimum value of 21[7] and the minimum pK value for cyclopentadiene should be slightly lower.[8] Consideration of this slight acidity of cyclopentadiene suggested that a reaction of cyclopentadiene with a metal halide in the presence of a hydrogen halide acceptor might be an alternate route for the preparation of bis-cyclopentadienyl-metal compounds, *e.g.*

$$2C_5H_6 + FeCl_2 + 2\ \text{Base} = (C_5H_5)_2Fe + 2\ \text{Base}\cdot HCl$$

We have found that such reactions do indeed give small yields of ferrocene and of bis-cyclopentadienyltitanium(IV) chloride,[9] $(C_5H_5)_2TiCl_2$. As hydrogen halide acceptors, triethylamine, diethylamine, pyridine and sodium methoxide have been used. The formation of $FeCl_2$–amine addition compounds that are insoluble in the solvents tried is a competing reaction that has thus far prevented good yields. Sodium methoxide seems to cause polymerization of the cyclopentadiene. It is, however, significant that bis-cyclopentadienyl-metal compounds are formed under these conditions; in the absence of a hydrogen halide acceptor, none of the desired product could be detected.

Experimental

(1) An equimolar mixture of $(C_2H_5)_3N$ and C_5H_6 was slowly added to anhydrous $FeCl_2$ with rapid stirring under a nitrogen atmosphere. Benzene was then added and the mixture was stirred overnight. The reaction mixture was filtered and the yellow filtrate was allowed to evaporate slowly. The yellow acicular crystals that separated were identified as ferrocene by infrared spectrum and melting point. A yield of about 4% was thus obtained. Variation of the base—$(C_2H_5)_2NH$, C_5H_5N, $NaOCH_3$—also gave similar yields. The use of ferrous acetate in place of the chloride with the above bases gave ferrocene but did not improve the yield.

(2) A benzene solution of $TiCl_4$ was added slowly with vigorous stirring to an equimolar mixture of $(C_2H_5)_3N$ and C_5H_6. The mixture was stirred overnight. Removal of the solvent from the red reaction mixture, extraction of the resulting residue with chloroform, and slow evaporation of the extracts yielded red crystals. Recrystallization from toluene gave pure $(C_5H_5)_2TiCl_2$, identified by its infrared spectrum. Yields of about 3% were obtained with triethylamine, diethylamine or pyridine. Again, serious competing reactions were the formation of insoluble $TiCl_4$–amine complexes and polymerization of the cyclopentadiene.

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The Pyrolysis of Methyl Ethyl Ketone Cyanohydrin Acetate

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The pyrolysis of unsymmetrical aliphatic acetates has been reported[1] to yield the olefin with the least number of alkyl groups attached to it.

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