

Kinetic Studies of Organometallic Compounds in Detail

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ABSTRACT: Kinetic data from reactions which are more complicated than simple first order processes can give linear plots of $\ln |M_\infty - M_t|$ against time (where M is a physical property of the reacting solution, such as absorbance or conductance). It is shown how these linear plots arise, and how the correct rate coefficients for complex reactions can be calculated from the pseudo-first-order rate coefficients, together with reagent concentrations and related information. This approach is useful for organometallic reactions, where there are often severe limitations on the experimental data that can be readily be obtained. Kinetic studies of the reaction of acetonitrile with $[(C_7H_8)M(CO)_3]$ ($M = Cr, Mo, \text{ or } W$) complexes show the third-order rate law, $\text{Rate} = k[\text{Complex}][\text{MeCN}]^2$. This order is explained in terms of a mechanism involving pre-equilibrium association between the complex and acetonitrile, followed by rate-determining addition of a second molecule of MeCN. The ease of cycloheptatriene displacement varies with the nature of the metal in the order $Mo > W > Cr$. In contrast, similar studies of the reaction of acetonitrile with the complex $[(C_6H_3Me_3)Mo(CO)_3]$ indicate the second-order rate law, $\text{Rate} = k[\text{Complex}][\text{MeCN}]$. The change in mechanism is rationalised in steric terms. Comparison with previous data for the corresponding reaction of acetonitrile with the cation $[(C_7H_7)Mo(CO)_3]^+$ suggest the order $C_7H_8 > C_6H_3Me_3 > C_7H_7$ for ease of displacement of π -bonding organic ligands from $[LMo(CO)_3]^{n+}$ ($n = 0$ or 1) species.

I. INTRODUCTION

Metals exist in several different ways, as the native metal, as simple salts, (i.e. NaCl) and as compounds with various types of ligands. These compounds may be either coordination compounds or organometallic compounds, in which the ligand forms covalent bonds with the metal. Coordination compounds are formed when an atom donates an electron pair to a metal atom. This is distinct from a covalent bond, where each atom donates a single electron to form the bond. The molecules that supply the atoms with which to form coordination compounds are called ligands. Ligands may be as simple as a water molecule, which binds to the metal through one of the two free electron pairs on the oxygen atom, or as complex as a hemoglobin, which contains a metalloporphyrin at its active site. The scope of this paper is confined to this subset of inorganic chemistry because this class of compounds comprises the majority of the metalloradiopharmaceuticals, metallopharmaceuticals, as well as most metalloproteins. An example of a simple coordination compound is $[CoIII(H_2O)_6]^{3+}$ (Fig. 1) where the a water molecule is located at each of the six vertices of the octahedron. Organometallic compounds are formed when covalent bonds between ligands and metal atoms are present. A simple example of an organometallic compound is $[Ni(CO)_6]_0$ (CO = carbon monoxide), where there are 6 CO molecules in an octahedral arrangement around the Ni0 core. Both coordinate and covalent bonds can be present in the same compound, as in $[Co(\text{methyl})(\text{dmg})_2(H_2O)]$ (dmg = dimethylglyoxime) (Fig. 2). In this octahedral compound there are five coordinate bonds, four N atoms in the equatorial plane and an apical water molecule, as well as a covalently bound methyl group at the other apex. This class of compounds has been used as models for vitamin B12.[1,2]

It is important to differentiate between the concepts of thermodynamic and kinetic stability. Thermodynamics (and log K values) tells you where the equilibrium lies. Kinetics, on the other hand, tells you how quickly you can achieve (or disrupt) the equilibrium. Thermodynamic stability is usually described in terms of the association constant (K) between the ligand and the metal. For example, $Cu^{2+} + DOTA \rightleftharpoons [Cu(DOTA)]^{2-}$ ($H_4DOTA = 1,4,7,10\text{-tetraazacyclododecane}$)
 $K = \frac{[Cu(DOTA)]^{2-}}{[Cu^{2+}][DOTA]}$

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II. DISCUSSION

From common positions critically considered is the notion of stability of isolated molecule of organometallic compound (OMC) as well as of the systems including OMC and products of their decomposition in various modular states of aggregation, energy (electronic structure stability) and space (molecular structure stability) factors of OMC stability and their manifestation under different conditions. Various aspects of OMC stability during their synthesis-decomposition processes proceeding under the conditions: thermal reactions with participation of uncharged (neutral) particles of OMC and decomposition products; electron impact or electric current effect with ionized particles participation, electromagnetic radiation effect are discussed. The necessity in complex solution of the OMC stability problem is pointed out. The effect of the nature of the metal M and the organic group R on the reaction of organometallic compounds RM (R = Ph, PhC triple bond C, C/sub 3/H/sub 7/, Allyl; M = Li, Mg, Zn, Cd, Cu Al), produced in situ from Grignard reagents or organolithium compounds and the respective salts, with p-iodoanisole in the presence of palladium complexes PdCl/sub 2/L/sub 2/ (L = PPh/sub 3/, MeCN, dppf) was studied. The organozinc and organoaluminum compounds react with a high degree of selectivity. In the reactions of C/sub 3/H/sub 7/M with p-MeOC/sub 6/H/sub 4/I the highest yield from cross-coupling is obtained with catalysis by the PdCl/sub 2/ (dppf) complex. This study can be partitioned into three major parts. The first part of the study focused on a comprehensive investigation of time-resolved step-scan Fourier-Transform infrared (TR-s2 -FTIR) spectroscopy of photogenerated transition-metal carbonyl radicals. The aim was to obtain the TR-s2 -FTIR spectroscopic data of the photogenerated seventeen electron transition metal carbonyl radicals by using three different methods of generating the radical species, namely, (1) 532nm photodissociation of metal-metal bond, (2) abstraction of hydrogen, halogen or methyl from monomeric transition metal carbonyl species, and (3) fast radical ligand substitution. The scope of study involved (1) developing the time-resolved step-scan Fourier-Transform infrared (TR-s2 -FTIR) spectroscopy experimental setup, (2) determining the IR bands and life-times of the detected radical species, (3) investigating the effect of the stereo-electronic of various phosphine ligands on the spectroscopy and kinetic of the transition metal carbonyl radicals, and (4) providing an assessment on the suitability of all three methods. The spectroscopic and kinetic data obtained from our experiments could help researchers to identify unknown relevant catalytic intermediates during the spectroscopic monitoring of the catalysis. Results of this study may help to shed light on a variety of transition metal carbonyl-catalyzed reactions in which the transition metal carbonyl radicals and their phosphine derivatives have been implicated as key reaction intermediates in solution.[3,4]

III. CONCLUSION

The rate constant for the methyl abstraction reaction of CpFe(CO)₂Me has been measured with the benzyl radical clock as $(1.1 \pm 0.2) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ at room temperature. Time-resolved Fourier-Transform Infrared (FTIR) absorption spectroscopy pointed towards the formation of the CpFe(CO)₂ radical upon benzyl abstraction. [5,6]. The main stable product has been established by a linear scan of the reaction mixture as Cp₂Fe₂(CO)₄ produced by the dimerization of the CpFe(CO)₂ radicals. The transition state structure for the abstraction process was also found at UB3LYP/6-311+G* level of theory to contain a planar CH₃ group. This methyl transfer process is calculated to be exothermic by 155 kJmol^{-1} and inhibited by a small activation barrier of 68 kJmol^{-1} [7,8]

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