



Reactivity of organometallic compounds and polarizability effect



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ABSTRACT

An elucidation of the factors determining the magnitude of the rate constants, k , is of primary importance in understanding organometallic reactivity. Nevertheless, the influence of substituents bound to the reaction centre on the k is poorly understood. In this work, the literature data on substituent influence on the $\log k$ values of reactions involving derivatives of Groups 5–10, 12–14, 16 elements (there are 25 series, in each of them the reaction centre being fixed, and the substituents varying in properties) have been analyzed, using the correlation analysis. Generally not only classic inductive, resonance, and steric effects, as well as the polarizability one have been first established to operate. The presence or absence of certain effects are dictated by the type of series. The polarizability effect is caused by a partial charge appearing on the reaction centre of the activated complex. The contribution of this effect ranges up to 50%. A knowledge of the substituent effects may give a better insight into organometallic reaction mechanisms.

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Introduction

It has long been known that the reactivity is one of the fundamental concepts in chemistry generally and in organometallic chemistry in particular. Under rigorous treatment the reactivity is measured by the rate constant k of a reaction. The most useful information on reactivity can be obtained through analysis of k values for so-called narrow reaction series. In general, the reactivity of organometallic compounds X_nBML_m depends on four variables, namely, M atom, the substituents X (Alk, Ph, AlkO, F, ...), the bridge B ($-C_6H_4-$, P atom, ...) between M and X_n , and the ligands L (CO, $\eta^5-C_5H_5$, ...). In compounds X_nML_m the bridge B is absent.

In narrow series, e.g. $X_3PMn(\eta^5-C_5H_5)(CO)_2COCH_3$, the three (M, B, and L) of the four (M, B, L, and X) variables are fixed. Because of this, the narrow series are ideally suited for elucidation of the mechanism of X substituent influence on the k values and thus on the reactivity. An investigation of such series has become the topic of a large body of research, see, for example [1–27]. Even a cursory examination of the findings of these investigations shows that in narrow series of organometallic compounds the rate constants k of different reactions depend strongly on the type of substituents X.

However, up to now, the question about the mechanism of substituent influence on k values remains open. Only in rare cases substituents X influence k via inductive and resonance effects, e.g. Refs. [2,11]. In many cases such explanation does not work as it has been strongly simplified.

There are reasons to assume that taking into account the polarizability effect will allow the problem to be solved. The first evidence for this effect has come from the study of ionic gas-phase reactions involving simple organic molecules [28–30]. Further investigations demonstrated that the polarizability effect has a profound influence on the parameters of the IR [31], NMR [32,33], EPR [34], NQR [35], UV–Vis electronic [36], ultraviolet photoelectron [37,38], X-ray photoelectron [39], and Mossbauer [40] spectra as well as on the bond lengths [41] and toxicity [42] of organometallic compounds. A necessary condition for arising this effect is initiation of the partial charge q on M atom and/or on bonds M–B and M–L. The charge q results from the chemical reaction, specifically the complexation [28–30], or the electromagnetic impact [31–42]. We emphasize that the effective approach to the study of the polarizability effect is the correlation analysis [31–42]. To the best of our knowledge up to now, no consideration has been given to the influence of this effect on the reactivity of organometallic compounds. Here, for the first time, we attacked this problem by a method of the correlation analysis of the rate constants of reactions involving the narrow series of compounds.

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¹ In memory of Professor Mikhail G. Voronkov.

Results and discussion

Out of a large body of the literature data we chose 25 reactions [1–25] (Table 1, series I–XXV) on several grounds. One of them is consideration of generality; these series contain 21 elements of Groups 5–10, 12–14, 16. Close examination of series I–XXV will be given below. Now we have to focus on three aspects of our major problem, namely, a general idea of the correlation analysis of the charged narrow series, the features of reactions I–XXV, and the correlation analysis of series I–XXV.

A general idea of the correlation analysis of the charged narrow series

According to Hammett's views, the correlation analysis is based on the concept of the linear free energy relationships (LFER) [43]. Let us consider the influence of substituents X on some properties P , which obey LFER concept, of the so-called charged classic and non-classic narrow reaction series having the general formulae 4-XC₆H₄R_c^q, XBR_c^q, and XR_c^q. Recall that in each of such series the reaction centre R_c and bridge B are fixed, whereas the substituents X vary.

The distinctive features of the charged classic narrow series 4-XC₆H₄R_c^q are a partial charge q on R_c, the large distance of X from R_c^q (a bridge B = C₆H₄ is long) as well as the absence of the through resonance effect (i.e. of the resonance interaction between X and R_c^q via the π-electron system) which is to say that the charge q is localized on R_c. In classic series only inductive and resonance effects of substituents X exert influence on the chemical and physical properties P :

$$P = P_0 + a\sigma_1 + b\sigma_R(\sigma_R^+, \sigma_R^-), \quad (1)$$

where σ_1 is a universal inductive constant of X substituents; σ_R , σ_R^+ , and σ_R^- are parameters characterizing the resonance effect of X in the presence of a small, large positive and large negative charge q , respectively [44,45].

In the charged non-classic narrow series XBR_c^q (a bridge B is shorter than –C₆H₄– fragment) and XR_c^q the mechanism of the intramolecular interactions is more complicated than that in the classic series 4-XC₆H₄R_c^q. In the case being considered not only the inductive and resonance effects but also the polarizability effect are in operation, e.g. Refs. [28–42]. The polarizability effect arises from an ion–dipole interaction between the charge q on R_c and the dipole moment induced by this charge in the substituent X. The energy E of such electrostatic interaction is expressed as follow:

$$E = -\alpha q^2 / (2l^4), \quad (2)$$

where α is the polarizability of the substituent X and l is the distance between the charge q and the induced dipole [46]. As is seen from Eq. (2), the energy E varies in proportion to l^{-4} , that is it depends strongly on the l value. In classic series 4-XC₆H₄R_c^q the distance l is long, that is why the polarizability effect is absent or probably is negligible. In the correlation analysis, instead of the energy E , the universal constants σ_α are convenient to use as a measure of the polarizability effect [28–42]. These constants for many substituents X are calculated by nonempirical quantum-chemical methods and normalized to the inductive σ_1 and resonance (σ_R , σ_R^+ , σ_R^-) constants of X [28–30,47]. On this basis, for the non-classic series XBR_c^q and XR_c^q Eq. (1) transforms to the following:

$$P = P_0 + a\sigma_1 + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha, \quad (3)$$

In series XR_c^q and probably in some series XBR_c^q the substituent X and reaction centre R_c are closely spaced. This can give rise to the steric effect. If the four effects (inductive, resonance, polarizability, and steric) influence the property P , the correlation equation takes the form:

$$P = P_0 + a\sigma_1 + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha + dE'_s, \quad (4)$$

where E'_s is a steric constant of substituents X [48,49].

The other symbols in Eqs. (1), (3) and (4) are identical.

It is vital to note that in specific cases narrow series 4-XC₆H₄R_c^q are not the classic series (as is discussed above) but the non-classic ones. This is caused by the through resonance effect, i.e. by the resonance interaction between X and R_c^q via the benzene ring, resulting in formation of the conjugated system. As a consequence the delocalization of the partial charge q and the arising of charge density on ring take place. The result of delocalization can be conceived as a decrease of the distance between X and R_c^q, causing the polarizability effect to arise [31,32,34,38]. Therefore the charged non-classic narrow series 4-XC₆H₄R_c^q obey Eq. (3).

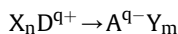
The central problem we face is to elucidate what substituent effects exert action on the rate constants k . To do this for 25 series each (I–XXV, Table 1) out of Eqs. (1), (3) and (4) we must choose so-called “the best fitting correlation equation”. It is probable that the type of such equation is dictated by the peculiarity of the series given. In this connection let us consider prerequisites for the correlation analysis of series I–XXV.

The features of reactions I–XXV

First it should be mentioned that according to Hammett's basic principle, in narrow series the logarithms of the reaction rate constants obey the LFER concept [43]. Hence if $P = \log k$, then equations of types (1), (3), and (4) must hold good for series I–XXV. As will be seen below this is true.

Let us consider other peculiarities of these series. In processes I–XXV σ constants characterize the capacity of substituents X to change the electron density on the reaction centre of the transition state. It is necessary to stress that the structure of the transition state of reactions I–XXV is a complicated problem [1–27] which calls for further investigation. For our purposes of prime importance is one aspect of the problem relative to complexation. As is known, the transition state represents the activated complex which is formed from reactants. As a result of the complexation, the initial and transition states differ in structure and thus in charge distribution [1–27].

To gain a better understanding of this difference, it is useful to mention briefly some of the peculiarities of donor–acceptor complexes X_nD·AY_m between bases X_nD (donor centre D is an atom having lone electron pairs) and acids AY_m (acceptor centre A is Main Group or transition metal having vacant orbitals), e.g. Refs. [50,51]. The complexation is accompanied by the electron density transfer from X_nD to AY_m and by the arising of the partial charges q on D and A atoms



The charges q can be partially delocalized over substituents X and Y. In narrow series of donor–acceptor complexes, for example, X₂O^{q+} → Al^{q-}Br₃ the charge q^+ induces dipoles in substituents X resulting in the polarizability effect [52]. This effect has a large influence on the physical properties of a great variety of intermolecular and intramolecular complexes [31–33,35–37,40–42].

As regards reactions I–XXV (Table 1), organometallic reactants incorporate elements of Groups 5–10, 12–14, 16 which are acceptor

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