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Correlation of the Reactivity of Organometallic Chlorides in the Oxidation of Magnesium with the Electronic Structure of the Organic Moiety

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Abstract—From the linear correlation of the chemical shift (^{19}F) in compounds R–C≡C–C_6H_4–F-*p* (reference PhF, solvent to-luene) with the Hammett σ_p constants of substituents R, the σ_p constants of organometallic substituents R [$Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$, $Cp(PPh_3)Ni$, Ph_2Bi, Ph_2Sb, Ph_3Sn] were calculated. The logarithm of the rate constant of magnesium oxidation with compounds RCl linearly correlates with the σ_p constants of the organometallic groups R.

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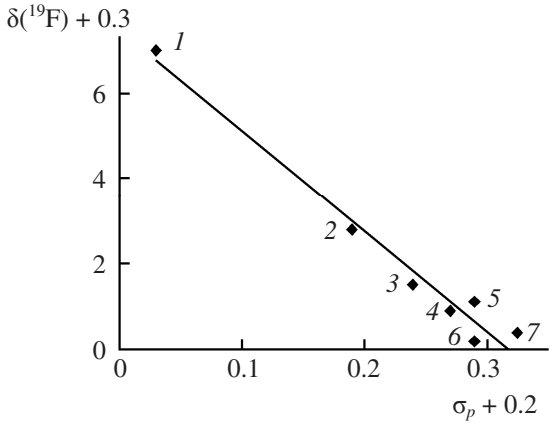
The mechanism of oxidative dissolution of metals in aprotic polar solvents, leading to the formation of Grignard reagent and related species, is the matter of permanent discussions [1–3]. At the same time, it was shown in [4–7] that such reactions obey the linear free energy relationship, and all the principles of the correlation analysis are valid for them. In particular, a set of systems with one variable parameter (substituent at the breaking bond, solvent, or substrate being oxidized) should be considered as a reaction series. According to the results reported in [3], redox systems of the type Mg–DMF–RCl [R = $Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$, $Cp(PPh_3)Ni$, Ph_2Bi, Ph_2Sb, Ph_3Sn] can be combined in one reaction series. In [7] we correlated the reactivity of the above chlorides toward magnesium with the ^{19}F NMR chemical shifts of compounds R–C≡C–C_6H_4–F-*p* (**I**) relative to PhF [8, 9]. Here we suggest to estimate the reactivity of organometallic chloride molecules toward magnesium from the Hammett σ_p constants of substituents R in compounds **I**. For this purpose, it is appropriate to express the chemical shift induced by fragments R via their inductive and resonance parameters.

Based on the well-known correlation of $\delta(^{19}F)$ for various derivatives of the aromatic series with the Hammett σ_p constants of substituents in the *p*-position of the benzene ring [10–12], we obtained the correlation of $\delta(^{19}F)$ with the parameters σ_p that also included compounds **I** (see figure).



Correlation of the chemical shift $\delta(^{19}F)$ of substituents in compounds R–C≡C–C_6H_4–F-*p* (relative to PhF used as reference; solvent toluene, 298 K) with the Hammett σ_p constants of substituents: (*1*) CH_3 , (*2*) C_6H_5, (*3*) $C(C_6H_5)_3$, (*4*) C_6H_4F-*p*, (5) $(C_6H_5)_3Pb$, (*6*) $(C_6H_5)_3Ge$, and (*7*) $(C_6H_5)_3Sn$.

The correlation equation for this dependence is as follows:

$$\delta(^{19}F) = -(22.40\pm1.35)\sigma_n + (0.09\pm0.02)$$
$$r\ 0.979,\ n\ 7. \quad (1)$$

The constants σ_p calculated from Eq. (1) for substituents R are as follows:

Substituent R	Hammett σ_p constant
Ph_2Bi	0.06
$Cp(CO)_3Mo$	–0.08
$Cp(CO)_3W$	–0.07
$Cp(CO)_2Fe$	–0.14
Ph_3Sn	0.15
$Cp(PPh_3)Ni$	–0.24

It should be noted that two-parameter Eq. (2) reflects the correlation of $\sigma(^{19}F)$ with the Hammett constants more adequately:

$$\delta(^{19}F) = -(33.25\pm1.15)\sigma_I - (10.23\pm0.88)\sigma_R + (2.40\pm0.06),$$
$$r\ 0.996, \quad (2)$$

where σ_I and σ_R are the inductive and resonance Taft constants of the substituents, respectively. However, the use of Eq. (2) and more complex polynomials [12] for determining the Taft constants of substituents from the known chemical shifts $\delta(^{19}F)$ is complicated by the fact that the number of variables is larger than the number of independent equations correlating them.

Nevertheless, Eq. (2) is useful for estimating the relative constants σ_I and σ_R when reliable experimental data on the chemical shifts are lacking or when it is necessary to pass from one reference (a substituent with zero value of σ_I or σ_R) to another.

The correlation of the logarithm of the rate constants of magnesium oxidation by compounds of various compositions and structures, including organometallic chlorides, in various solvents, with the σ_p constants of substituents can be described by Eq. (3):

$$\text{Log } k = \log k_0 + \rho\sigma_n. \quad (3)$$

We obtained the specific equations of type (3) for five systems:

(a) Mg + RCl + diethyl ether, R = FC_6H_4, Ph, MeC_6H_4, $MeOC_6H_4$, $NH_2C_6H_4$; T 273 K; log k_0 = –1.93; ρ 5.44; r 0.973.

(b) Mg + RBr + diethyl ether, R = FC_6H_4, ClC_6H_4, Ph, $CF3C_6H_4$, MeC_6H_4, $MeOC_6H_4$, $NH_2C_6H_4$; T 273 K; log k_0 = –1.87; ρ 3.36; r 0.989.

(c) Mg + RBr + THF, R = FC_6H_4, ClC_6H_4, Ph, $NH_2C_6H_4$, BrC_6H_4; T 273 K; log k_0 = –1.32; ρ 1.14; r 0.969.

(d) Mg + RBr + di-*n*-butyl ether, R = FC_6H_4, ClC_6H_4, Ph, EtC_6H_4, *t*-BuC_6H_4; T 273 K; log k_0 = –2.43; ρ 5.37; r 0.991.

(e) Mg + RCl + DMF, R = $Cp(CO)_3W$, $Cp(CO)_3Mo$, $Cp(CO)_2Fe$, Ph_2Sb, Ph_2Bi, $Cp(PPh_3)Ni$; T 293 K; log k_0 = –2.22; ρ 10.93; r 0.985 [3].

When calculating the coefficients of Eq. (3) for series (a)–(d), we used the rate constants of magnesium oxidation taken from [4, 5].

Equation (3) is valid for oxidative dissolution of metals in various aprotic media. However, in contrast to the classical Hammett relationship, it is also valid for oxidants whose organic groups R are not directly bonded to the benzene ring. The quantities $\delta(^{19}F)$ and σ_p reflect the same electronic effects of substituents R in the conjugated aromatic system. Therefore, using their linear correlation with Eq. (1), it is possible to eliminate from $\delta(^{19}F)$, measured in σ_p units, the contribution corresponding to the common aromatic fragment C≡C–Ph.

The absolute term in Eq. (3), firstly, corresponds to the logarithm of the rate constant of the reaction in which the oxidant is PhCl or PhBr and, secondly, depends on particular halogen (Cl or Br). The choice of these compounds as reference oxidants is governed by the fact that therein the substituent R in the *p*-position of the benzene ring in them is hydrogen atom whose σ_p is 0. These phenyl halides are convenient reference substances for estimating the reactivity of oxidants with any substituents R, including the above-indicated organometallic fragments.

For reaction series (a)–(e), ρ > 0. The highest ρ is observed in the system with DMF as solvent. As ρ is the measure of the polarity of the transition state, it can be concluded that the activated complex formed in DMF has the highest dipole moment. This can be accounted for by the strong polarizing effect of the solvent on the R–Cl bond which is broken in the oxidant molecule. Furthermore, the DMF molecule (μ 4.2 D) can stabilize the dipoles $Mg^{\delta+}\cdots Cl^{\delta-}$ and $Mg^{\delta+}\cdots R^{\delta-}$ in the activated complex forming on the

magnesium surface. In this case, the reaction rate should be limited by the step in which the oxidant acts as electrophilic agent. This trend is the most pronounced in system (e). Hence follows that the electron density transfer from the halogen atom in the oxidant molecule to the outer molecular orbitals of the metal surface in the course of adsorption does not control the rate of the substrate oxidation.

For the organic chlorides considered in this study, under equal other conditions [see triad (b), (c), (d), or pair (a), (e)], ρ is larger than for the related bromides.

This may be due to the higher electronegativity of Cl compared to Br [13]. Therefore, the polarity of the R···Cl and Mg···Cl bonds and of the activated complex is, on the whole, higher than for the bromide analogs. It should be noted in conclusion that our concept of magnesium oxidation is valid only for cases when all the systems under consideration, (a)–(e), form a common kinetic series.

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