ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 7, pp. 1155–1157. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © S.V. Panteleev, S.V. Maslennikov, A.N. Egorochkin, I.V. Spirina, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 7, pp. 1072–1074.

Correlation of the Reactivity of Organoelement Chlorides in Metal Oxidation in Aprotic Media

S. V. Panteleev[a], S. V. Maslennikov[a], A. N. Egorochkin[b], and I. V. Spirina[a]

[a] *Research Institute of Chemistry, Lobachevskii Nizhni Novgorod State University,*
pr. Gagarina, 23, korp. 5, Nizhni Novgorod, 603950 Russia
e-mail: spirina@ichem.unn.runnet.ru
[b] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russia*

Received October 16, 2006

Abstract—The reactivity of RMCl compounds [RM = $Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$, $Cp(PPh_3)Ni$, and Ph_2Bi] used as oxidants in reactions with metals in aprotic media was assessed to establish that the electron density of the metal atom in the RM group is linearly related to the total electronegativity of this group. The resulting electron densities correlate with the log rate constants of magnesium oxidation with the RMCl compounds in DMF. The reactivity of the oxidants in the organometallic chloride–compact metal–solvent system is a function of the physicochemical properties of the medium.

DOI: 10.1134/S1070363207070031

There has been certain progress in the field of metal dissolution in aprotic media [1–3], which allows qualitative correlations between the reactivity of oxidants and the physicochemical properties of the medium. In this connection of importance is to quantitatively correlate the kinetic parameters of the reactions and the nature of the reagents.

The polarity and length of a bond involved in reaction, molecular radii of reagents, and electronic effects of substituents are used as parameters directly related to the reactivity of compounds in various systems [4, 5].

Treating the results in [3] we revealed a linear correlation between the log rate constants of magnesium oxidation in DMF with compounds RMCl [RM = = $Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Fe$, $Cp(PPh_3)Ni$, Ph_2Bi] (**I**) and the polarity of the M–Hlg bond, estimated from the $\delta(^{19}F)$ values [6] of compounds $RM–C≡C–C_6H_4F$-*p* (**II**), measured relative to PhF.

The dependence of log *k* vs $\delta(^{19}F)$ (see figure) is described by Eq. (1).

$$\log k = -1.86 - 0.88\delta(^{19}F), \qquad (1)$$
$$r\ 0.992.$$

The ^{19}F chemical shifts of compounds **II** with various RM groups, used for M–Hlg polarity assessment, are known for a limited number of compounds [7]. In this connection we considered it expedient to extend the range of oxidants whose polarity would adhere to Eq. (1). One of the possible ways to approach this problem is to correlate $\delta(^{19}F)$ of compounds **II** with parameters relating to atomic electron density distribution in the RM fragment. For such characteristics one can use the electronegativity of molecular fragments, polarizability, or bond stretching frequencies [7]. These parameters should be readily determined for a wide range of structurally related compounds.

The chemical shifts of RM fragments (M is a transition metal), lacking from the literature, can be fairly correctly estimated by Eq. (2).

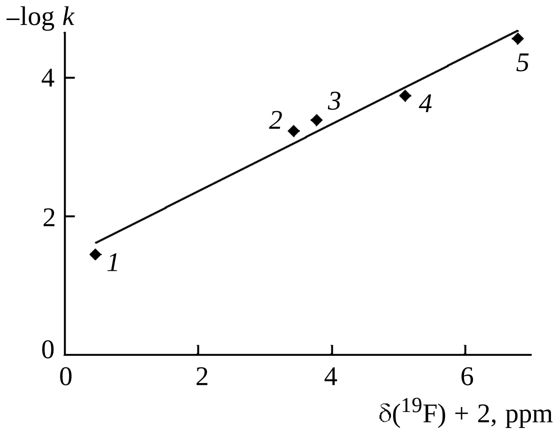
$$\delta(^{19}F) = 2.72\chi(1 - 0.4n) + 2.05, \qquad (2)$$
$$r\ 0.988.$$

Here χ is the relative Pauling electronegativity [8] of the metal atom and *n*, number of carbonyl or triphenylphosphinyl ligands attached to the metal atom.

The same correlation for main group metals has Eq. (3), where *m* is the number of phenyl groups attached to the metal atom.

$$\delta(^{19}F) = 2.30(\chi - 0.4m) - 4.45, \qquad (3)$$
$$r\ 0.960.$$

Equations (2) and (3) allow one to estimate $\delta(^{19}F)$ for compounds with various RM groups and, using Eq. (1), to estimate the rate constants of magnesium



Plot of the log rate constans of magnesium oxidation with RMCl in DMF vs. the $\delta(^{19}F)$ values of compound **II**, measured relative to PhF. RM: (*1*) Ph_2BiCl, (*2*) $Cp(CO)_3WCl$, (*3*) $Cp(CO)_3MoCl$, (*4*) $Cp(CO)_2FeCl$, and (*5*) $Cp(PPh_3)NiCl$.

oxidation with organometallic chlorides containing such groups.

It was previously shown [9] that the dependence of metal oxidation rate on medium properties is described by Eq. (4).

$$\log W = A_0(a + bB + cZ + d\delta^2 + e\sigma). \quad (4)$$

Here A_0 is the constant of the oxidized metal; *B*, *Z*, δ^2, and σ, solvent parameters (Koppel–Palm nucleophilicity, polarity, Hildebrand solubility parameter, and van der Waal radius, respectively) [10–12]; *a*, *b*, *c*, *d*, and *e*, coefficients relating to the contributions of the medium properties and depending, probably, on oxidant properties. The *a*, *b*, *c*, *d*, and *e* coefficients correlate with $\delta(^{19}F)$ for compounds **II**. This means that these parameters are functions of the M–Cl bond polarity in the oxidant molecules. Therewith, the nature of the ligand and oxidized metal have no effect on *a*, *b*, *c*, *d*, and *e*. Their dependence of the $\delta(^{19}F)$ values of compounds **II** with various RM groups can be represented by equations set (5).

$$\log \prod_{ox,i} = \alpha_i\delta(^{19}F) + \beta_i. \quad (5)$$

Here $\prod_{ox,i}$ is the coefficient at the *i*th property of the solvent in Eq. (4); $\delta(^{19}F)$, chemical shift of compound **II**; and α_i and β_i, regression coefficients.

Calculations gave the following α_i and β_i values.

Coefficients:	*a*	*b*	*c*	*d*	*e*
α:	0.19	0.20	0.20	0.19	0.20
β:	–0.32	–2.20	0.84	1.11	–1.99

As follows from the resulting data, the sensitivity of α to chemical shift is constant for all the oxidants considered in the present work, whereas β in Eq. (5) both in value and in sign. These results show that each of the *a*, *b*, *c*, *d*, and *e* parameters is a function of the same oxidant parameter, specifically M–Cl bond polarity. Therefore, these coefficients differ from each other by a constant $\exp\beta_i$ whose presence is due to the fact that the *B*, *Z*, δ^2, and σ values in Eq. (4) have different orders.

Equations set (5) is similar in form to Hammett–Taft equations. The oxidant parameter $\delta(^{19}F)$ relates to the reactivity of the M–Cl bond in metal dissolution reactions in aprotic media. The value of this parameter shows the relative reactivity of RMCl in a given solvent with respect to the oxidative ability C_6H_5Cl as reference. The coefficient α is a constant of the RMCl oxidant series and the solvent used. The α value is similar to the ρ value in the Hammett equation and is probably related to the mechanism of the process, in particular, to features of reagent adsorption on a solid surface. The coefficient β_i relates to the contribution of individual medium properties (nucleophilicity, polarity, etc.) into the overall reaction rate for the case when the oxidant in PhCl.

Since the chemical shift of the RM group in compounds **II** is linear in the electronegativity of metal M [Eqs. (2) and (3)], then, obviously, the coefficients *a*, *b*, *c*, *d*, and *e*, too, will be linear in χ.

REFERENCES

1. Rogers, H.R., Deutch, J., and Whitesides, G.M., *J. Am. Chem. Soc.*, 1980, vol. 102, no. 1, p. 226.
2. Rogers, H.R., Rogers, R.J., Mitchel, H.L., and Whitesides, G.M., *J. Am. Chem. Soc.*, 1980, vol. 102, no. 1, p. 231.
3. Maslennikov, S.V., *Doctoral (Chem.) Dissertation*, Nizhny Novgorod, 2005.
4. Fedorov, L.A., *Spektroskopiya YaMR metalloorganicheskikh soedinenii* (NMR Spectroscopy of Organometallic Compounds), Moscow: Nauka, 1984.
5. Moelwyn-Hughes, E.A., *The Chemical Statics and Kinetics of Solutions*, London: Academic, 1971.
6. Peregudov, A.S. and Kravtsov, D.N., *Appl. Organomet. Chem.*, 2001, vol. 15, no. 3, p. 23.
7. Kravtsov, D.N., *Metalloorg. Khim.*, 1989, vol. 2, no. 1, p. 157.
8. Emsley, J., *The Elements*, Oxford: Clarendon, 1989.

9. Panteleev, S.V., Maslennikov, S.V., Egorochkin, A.N., and Vakulenko, V.Yu., *Zh. Obshch. Khim.*, 2007, vol. 77, no. 6, p. 912.

10. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, Weinheim: VCH, 1988, 2nd ed.

11. Burger, K., *Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents*, Budapest: Akad. Kiadò, 1983.

12. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solutions*, Wien: Springer, 1968.