ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 6, pp. 1004–1007. © Pleiades Publishing, Ltd., 2007.
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Solvent Effect on Metal Oxidation Rates in Aprotic Media

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Received August 3, 2006

Abstract — A correlation between the rates of oxidation of metals with organometallic chlorides in aprotic media and the physicochemical properties of the solvents was established. An equation fitting the experimental data for ten reaction series was suggested. The kinetic parameters of oxidation of cadmium with diphenylbismuth chloride in aprotic media, calculated with the correlation equations, coincide with the experimental data.

DOI: 10.1134/S1070363207060084

Oxidation of metals with organometallic compounds in aprotic solvents is an example of classical heterogeneous reactions. Numerous papers deal with this subject [1–4]. Therefore, quantitative interpretation of the previously obtained experimental results is a topical problem.

One of methods for revealing semiempirical relationships between kinetic characteristics of systems and properties of the medium is correlation analysis [5, 6]. For heterogeneous systems, in which reactions are complicated by processes occurring on the phase boundary, such relationships were found in [7, 8] in the course of studying oxidation of magnesium with *p*-substituted phenyl halides; a correlation was revealed between the kinetic characteristics of the reactions and the Hammett constants of substituents in the aromatic ring. The mechanism and type of control of the reaction were suggested on the basis of these data.

The use of polar aprotic solvents considerably facilitates the synthesis of metal-containing and organometallic compounds [9, 10]. Kondin [11] noted that the dependence of the metal oxidation rate on the solvent donor number DN_{SbCl_5} [12] passes through an extremum. It should be noted that the data of the previously published papers [4, 9, 10] also suggest the presence of an extremum in the dependence $W = f(DN_{SbCl_5})$.

It is known [4, 11] that functionally related compounds and even homologs differing in the donor number behave differently. For example, in ethyl acetate magnesium is oxidized with ethyl bromide, whereas in methyl acetate the reaction does not occur under similar conditions; in acetonitrile zinc and cadmium react with ethyl iodide, whereas in benzonitrile the reaction does not occur [11], etc.

The kinetics of reactions of metals with oxidants RMCl [RM = $Cp(CO)_3W$, $Cp(CO)_3Mo$, Ph_2Sb, Ph_2Bi] in aprotic media were studied in [13], and the dependences of the relative rates of these processes on the solvent donor number were determined (Table 1).

In the course of metal oxidation, a polar solvent can stabilize the forming organometallic compound or dissolve the film of reaction products preventing the access of reagents to the surface. However, it is known [14] that organomagnesium compounds can also be prepared in inert solvents or even without a solvent. Attempts to correlate the extremum in the dependence $W = f(DN_{SbCl_5})$ with the solubility of metal halides formed in the process failed [15]. In some cases, the oxidation rate was the highest in solvents in which the solubility of the corresponding halide was the lowest.

It is known [16] that the dependence of the adsorption of various organic compounds on metal and metal oxide surfaces on the ionization potential of the sorbate passes through an extremum. At the same time, the correlation between the solvent donor number and ionization potential is linear [12]. It can be anticipated that the dependence $W = f(DN_{SbCl_5})$ [13] will be described by the expression $W = f(I)$, where I is the ionization potential of the solvent molecule. At $I = I_{res}$ (resonance ionization potential) [16], the metal

Table 1. Relative oxidation rates of metals in relation to the solvent donor numbers at c_{ox}^0 0.2 M and T 293 K

Solvent	Reaction system[a]								
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
p-Xylene	0.05	0.00	0.02						
Dioxane		0.03	0.09	0.11			0.02	0.01	
Ethyl acetate	0.25	0.10				0.08			0.09
Diethyl ether			0.12	0.16					
THF	0.59	0.18	0.18	0.46	0.46	0.15			0.13
Diglyme		0.34	0.41	0.54	0.49	0.31	0.15	0.12	
DMF	1.00	0.61	0.54	1.00	1.00	0.60	1.00	1.00	0.33
DMSO	0.43	1.00	1.00	0.72	0.83	1.00	0.74	0.79	0.89
Pyridine	0.36	0.37	0.40	0.02		0.41	0.65	0.66	1.00
HMPA	0.16	0.12	0.18	0.09	0.10	0.20	0.04	0.07	0.06

[a] (**I**) Mg, $Cp(CO)_3WCl$; (**II**) Mg, Ph_2SbCl; (**III**) Mg, Ph_2BiCl; (**IV**) Zn, $Cp(CO)_3MoCl$; (**V**) Zn, $Cp(CO)_3WCl$; (**VI**) Zn, Ph_2SbCl; (**VII**) Cd, $Cp(CO)_3MoCl$; (**VIII**) Cd, $Cp(CO)_3WCl$; and (**IX**) Sn, $Cp(CO)_3MoCl$.

oxidation rate will be the highest. Based on data from [17], this fact can be attributed to the electron transfer from the highest occupied molecular orbital of the adsorbate to the lowest unoccupied orbital of the adsorbent.

The dependence of the rate of metal oxidation with various oxidants on the solvent donor number is influenced by numerous factors. For the reaction series studied in [13], there is a good correlation (1) of the reaction rate with solvent properties:

$$\log W = A_0(a + bB + cZ + d\delta^2 + e\sigma), \qquad (1)$$

where B is the Koppel–Palm nucleophilicity of solvent molecules [12]. This parameter reflects the capability of solvent molecules for coordination (i.e., donor–acceptor) interactions. The solvent molecules can interact not only with oxidant molecules but also with the metal surface, which is a polycentral acceptor [18]. The quantity Z takes into account electrostatic interactions in the system:

$$Z = \frac{n^2 - 1}{n^2 + 2} + \frac{\varepsilon - 1}{2\varepsilon + 2}. \qquad (2)$$

The terms $(n^2 - 1)/(n^2 + 2)$ and $(\varepsilon - 1)/(2\varepsilon + 1)$ in a certain interval of n and ε vary in the same direction, which suggests the possibility of including only one of these terms in Eq. (1). Makitra et al. [19–21], used both these terms in combination in multiparameter equations. The validity of this approach is confirmed by the data [22] demonstrating direct correlation of the enthalpy of interaction of certain compounds (including halides of various compositions and structures) in aprotic media with the quantity Z.

The parameter δ^2 is the Hildebrand solubility parameter squared, and σ is the van der Waals radius of the free ligand molecule [22]. The parameter A_0 reflects the influence exerted on the overall reaction rate by the crystal lattice energy and first ionization potential of the metal being oxidized. Inclusion into the overall equation of each of the parameters increases the correlation coefficient, which indicates that the oxidation rate directly correlates with all these properties.

The coefficients *a, b, c, d*, and *e* are proportional to the contributions of the respective solvent properties and, most probably, correspond to the oxidant parameters that exert the strongest effect on the reaction rate. In view of these notes, expression (1) can be transformed into (3), where P_{ox} is the oxidant parameter for a given ligand property P_L:

$$\log W = A_0\Sigma(P_{ox}P_L)_i. \qquad (3)$$

It was noted in [13] that one of the major factors in the effect of a coordinating solvent on the reaction course is the transfer of the electron density from an adsorbed ligand molecule to the metal, because the electron work function from the metal depends on the donor power of the solvent adsorbed on a solid surface [23]. This is probably caused by the effect of the adsorbed species on the energy levels of the active centers of the surface. At the same time, donor solvents interact with acceptor molecules and ions to form solvates whose stability increases with an increase in the Gutmann donor numbers [18].

As the solvent interacts not only with an oxidant but also with a substrate, each solvent property in

Table 2. Coefficients in Eq. (1) for various redox systems (c^0_{ox} 0.2 M, T 293 K)

M	Coefficient	$Cp(CO_3)MoCl$	$Cp(CO)_3WCl$	Ph_2SbCl	Ph_2BiCl
Mg	*a*		1.003	2.001	0.177
	b		0.013	0.027	0.003
	c		13.836	–29.438	–3.408
	d		26.740	54.294	6.283
	e		0.021	0.043	0.005
Zn	*a*	1.000	0.843	2.002	
	b	0.013	0.011	0.026	
	c	–14.613	–12.313	–29.056	
	d	26.973	22.748	53.583	
	e	0.022	0.018	0.043	
Cd	*a*	1.000	0.981		0.238
	b	0.013	0.012		0.003
	c	–13.867	–13.625		–3.408
	d	25.527	25.085		6.283
	e	0.020	0.020		0.005
Sn	*a*	1.000			
	b	0.015			
	c	–16.040			
	d	29.615			
	e	0.024			

Eq. (1) reflects this dual behavior. For example, the nucleophilicity favors an increase in the reaction rate throughout the donor number scale, as indicated by the positive sign of *b*. The negative contribution of *Z* is most probably due to the fact that, in solvation of an oxidant with the solvent molecules, the extent of ionization of the M–Cl bond grows with an increase in the solvent dielectric permittivity.

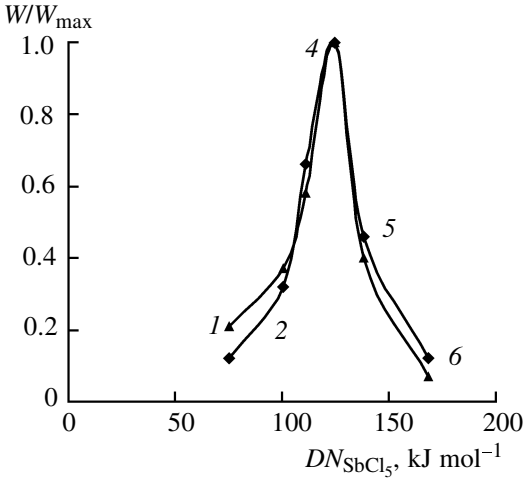
The contributions of particular solvent properties to the logarithm of the oxidation rate are different and strongly depend on the electronic and steric structure of the molecules; however, it is difficult to make an unambiguous conclusion about the effect of these properties on $\log W$ in Eq. (1), because the solvent participates in both solvation and adsorption processes. For example, the acetonitrile molecule has the smallest radius (σ) among the solvent molecules considered, but this factor in Eq. (1) cannot be neglected, because the distribution of the adsorbed CH_3CN molecules on the metal surface is also a function of σ.

This conclusion should be extended to all the properties included as parameters in Eq. (1). Therefore, each coefficient of this expression contains volume and surface constituents, i.e., $a = f(a_s, a_v)$, $b = \varphi(b_s, b_v)$, etc. To separate these constituents, it is necessary to obtain an experimental dependence of the equilibrium constants and enthalpies of adsorption or solvation of the reagents on the same solvent properties.

The relative rates of metal oxidation were calculated by Eq. (1) for systems with Mg, Zn, and Cd as substrates and $Cp(CO)_3MoCl$, $Cp(CO)_3WCl$, Ph_2SbCl, and Ph_2BiCl as oxidants.

The results given in Table 2 were obtained by solving a system of linear equations (1) in which both the coefficients *a, b, c, d*, and *e* and the parameter A_0 were unknown. The coefficients found for $Cp(CO)_3 \cdot MoCl$ were normalized with respect to parameter *a*; in so doing, the polynomials in Eq. (1) for the metals being oxidized were essentially identical. For the other oxidants, the coefficients *a, b, c, d*, and *e* were calculated similarly. As for A_0, this quantity is determined exclusively by the nature of the metal being oxidized and therefore is the same for all the oxidants used: 39.9 for Mg, 49.48 for Zn, 485.46 for Cd, and 45.44 for Sn.

Equation (1) reproduces the shape of the experimental dependence $W = f(DN_{SbCl_4})$ for systems **I**–**IX** (Table 1). With this equation, it is possible to choose a solvent in which the oxidation rate in the system metal–oxidant–ligand will be the highest. This is important for efficient control of the reaction. For example, for the system Cd–Ph_2BiCl–donor solvent, the coefficients *a, b, c, d*, and *e* were calculated from the experimental data on the oxidation of magnesium with diphenylbismuth chloride in aprotic solvents (Table 2). The results of the calculation of the relative



Relative rate of cadmium oxidation with diphenylbismuth chloride as a function of the solvent donor number. Squares, calculation; triangles, experiment; (*1*) THF, (*2*) diglyme, (*3*) DMF, (*4*) DMSO, (*5*) pyridine, and (*6*) HMPA.

rates of cadmium oxidation with diphenylbismuth chloride, as functions of the solvent donor number, are plotted in the figure.

The correlation coefficient for the calculated and experimental values for this system is 0.986. The pair correlation coefficients for particular parameters are as follows:

$$r_B\ 0.796,\ r_Z\ 0.534,\ r_{\delta^2}\ 0.377,\ r_\sigma\ 0.397.$$

Expression (1) makes it possible to determine by calculation an aprotic medium in which the metal oxidation rate will be the highest, under equal other conditions.

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