

QUANTITATIVE DESCRIPTION OF SOLVENT EFFECTS ON THE KINETICS OF METAL COMPOUNDS BY A FOUR-PARAMETER EQUATION

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Abstract. Correlations between 18 parameters expressing acidity, basicity, and polarity for 66 solvents were calculated. Four mutually independent parameters with clear physico-chemical meaning, gas phase acidity (deprotonation enthalpy, DPE), gas phase basicity (proton affinity, PA), polarizability ($P = (n^2 - 1)/(2n^2 + 1)$), and squared Hildebrand's parameter (δ^2_{H}) were selected for a multiparameter equation. Correlations of rate logarithms for 39 reactions at metal centres with this equation and, for comparison, equations proposed by Koppel and Palm and by Kamlet and co-authors were carried out. In most cases the new equation described kinetic data satisfactorily; however, more correlations with different data are needed to prove its general validity. Correlations were affected by insufficient number of PA and DPE values. Absence of the traditional acidity parameter did not cause weaker correlations. Possible interpretations of the parameters in the new equation were proposed.

Key words: solvent effects on kinetics, multiparameter equation, organometallic chemistry, metal complex chemistry.

INTRODUCTION

Multiparameter equations

The most remarkable success in quantitative description of solvent effects on the kinetics and other physico-chemical properties has been gained using linear free energy relationships [1] with multiple mutually independent empirical and physical parameters expressing liquid-phase conditions in terms of distinctive properties (acidity, basicity, and polarity) of individual solvents [1–3].

A four-parameter equation was proposed by Koppel and Palm [2]. In this equation the specific and nonspecific interactions between solvent and solute are separated:

$$A = A_0 + yY + pP + eE + bB,$$

where A is the value of a solvent-dependent physico-chemical property; A_0 is its value for the gas phase; $Y = (\epsilon - 1)/(\epsilon + 2)$ and $P = (n^2 - 1)/(n^2 + 2)$ are nonspecific parameters characterizing solvent polarization and polarizability, respectively. According to classical electrostatic theory, $E = E_T(30) - 25.10 - 14.84Y - 9.59P$, where $E_T(30)$ is Reichardt's parameter and $B = \Delta\nu_{OH}$ (solvent shifts of the ir stretching frequencies of the OH-band in phenol or, earlier, of the OD-band in MeOD) are specific parameters, measuring Lewis acidity and basicity, respectively. Lowercase letters designate the susceptibilities of a reaction to the respective parameters.

Another equation was proposed by Kamlet et al. [3]. Their equation uses statistically averaged parameters from several electronic spectra of solvatochromic indicators:

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi,$$

where α , β , and π^* are parameters for hydrogen bond donicity, hydrogen bond acceptivity, and polarity, respectively; δ_H is the Hildebrand solubility parameter; δ is polarizability correction term; and ξ is discontinuous co-ordinate covalency parameter; s , d , a , b , h , and e are susceptibilities of a reaction to the respective parameters.

A three-parameter equation was proposed by Mayer (cited in [1]):

$$\Delta\Delta G = a\Delta DN + b\Delta AN + c\Delta\Delta G_{\text{vap}},$$

where ΔG represents Gibbs energy change in the solvent, DN and AN are parameters for Lewis basicity and acidity, respectively; ΔG_{vap} is Gibbs energy change of vaporization of the solvent. These are all expressed in reference to acetonitrile. The a , b , and c terms are susceptibilities of a reaction to the respective parameters.

Generally, one or more terms drop out from a multiparameter equation due to their statistical insignificance. If a parameter has a physical meaning and describes the solvent effect to a great extent, it is believed that the respective physico-chemical interactions are responsible for different solvation of reactants and activated complexes in chemical reactions.

In several cases, only parameters derived from factor analysis (FA) or principal component analysis (PCA) are used in multiparameter approaches. These describe different data surprisingly well if the initial parameters are properly chosen, though they are unevenly associated with certain physical interactions.

Nevertheless, it can be concluded on the basis of FA and PCA that the number of parameters needed for the description of solvent effects on physico-chemical properties is small, most likely equal to three [4]. Though, by another well motivated opinion, nine parameters are needed [5]. For example, instead of five basicity-dependent properties of 22 organic non-hydrogen bond donor (non-HBD) solvents PCA gives only two principal components, which describe over 95% of the information. One is colinear with the gas phase proton affinity once corrected for the enhanced (molecular) polarizability effect, the other correlates with electrostatic properties [6]. For more examples, see references [1, 4].

Solvent effect on the reactions with metal compounds

Strong and often unpredictable solvent effects on reactions at metal centres make their investigation and description intriguing though highly complicated. The structure of reactants can be very different in different solvents, thus making the reaction rates in them incomparable. In many cases the reaction mechanism is not clearly stated, allowing for the possibility that different processes are preferred in different solvents. Organometallic compounds often form dimers and other self-associates, particularly in inert solvents. Inorganic salts form solvated separate ions, solvent-separated ion pairs or contact ion pairs, triplets, etc. Most solvent parameters characterize pure individual solvents. Interactions between metal compounds and donor solvents are usually strong, HBD or HBA (hydrogen bond acceptor) ability and electrostatic properties of a solvent can be greatly influenced by a polar solute. A partially ionic metal compound can associate with donor or acceptor solvent molecules or break the structure of amphiprotic solvents. A solvent can simultaneously be a reactant, a substitute of a reactant, a competitor, a catalyst, and a reaction medium.

Petrosyan [7] found solvent effects on organometallic chemistry to be very complicated and depend on several factors: the type of reaction under investigation, the nature of the organometallic compound and the substrate, their solvation, the solvation of the transition state, and the polarity of the solvent. Hydroxylic solvents can form complexes with reagents both by the solvation of metal atoms and by means of intermolecular hydrogen bonds. In nonpolar solvents some reactions can be substantially catalyzed by the polar products, which is explained by the increasing polarity of the medium [7]. A few attempts have been made to describe solvent effects on organometallic and metal complex chemistry by multiparameter equations. On the basis of the short reaction series conclusions cannot be drawn with absolute certainty; however, correlations may offer some valuable information on the reaction mechanism. In several studies [8–12], single rate logarithms have been correlated with linear and nonlinear multiparameter equations. There is practically no extensive review of the quantitative description of the reactions at metal centres by multiparameter equations.

METHODS

Correlation analysis in this work was performed by Statgraphics™ Version 5.0. All correlations were made at confidence level 0.95. Kinetic data on the reactions at metal centres in at least five individual solvents were investigated. Electrochemical data and data where the estimated mechanism (in terms of the order of reaction, solvation number, complex geometry, or reaction pathway) was very different in different solvents, as well as data on reactions in complicated systems with many participating reagents and diffusion-controlled rate constants, were excluded. Correlation coefficients between solvent parameters in Table 2 were calculated by procedure *Q. Multivariate Methods 1. Correlation Analysis*. Correlations between natural logarithms of reaction rates or similar data and the multiparameter equations in Table 3 were calculated by procedure *K. Regression Analysis 3. Multiple Regression*, choosing between different expression possibilities by comparing (adjusted for degrees of freedom) squared multiple correlation coefficients (R^2), standard errors (s), significances by Student's t -test, absence or presence of parameter values, and Durbin-Watson characteristics critically, considering results of procedures *Q. Multivariate Methods 1. Correlation Analysis* and *K. Regression Analysis 4. Stepwise Variable Selection*. In most cases, only significant parameters and constants ($p < 0.05$) were considered descriptive.

BRIEF CHARACTERIZATION OF REACTIONS

The following reactions were considered in this work:

Reactions with M-C bond cleavage:

1. k of reaction between dipropylmagnesium and pinacolone (solvents 40, 47, 49, 50, 52, 53, 54, see Table 1) [12]
2. r at 298.2 K as relative rate of destruction of cyclohexylmercury perchlorate (3, 13, 16, 21, 27, 43, 60) [13]
3. k_2 ($M^{-1}s^{-1}$) at 293.2 K of (phenylmethyl)mercury chloride iodolysis (in the presence of cadmium iodide catalyst) (5, 10, 11, 13, 16, 27) [13]
- 4.-9. k_2 ($M^{-1}s^{-1}$) of alkyltin iodolysis, tetramethyltin, tetrapropyltin, ethyltrimethyltin, butyltrimethyltin, dimethyldipropyltin, and triethylmethyltin, respectively (11, 16, 21, 39, 45) [14]
10. ΔG^\ddagger (kcal mol $^{-1}$) at 293.2 K of tetramethyltin + methyltin trichloride substitution (ΔG^\ddagger for two nonpolar solvents excluded because of different mechanism) (5, 10, 11, 12, 21) [7]

Other organometallic reactions:

11. r at 307.2 K as relative rate of substitution of trimethyltin chloride + methylthiotrimethyltin (37, 39, 45, 48, 57) [15]

12. k_1 (s^{-1}) at 333.2 K of reductive elimination of ethane from *cis-bis*(diphenylmethylphosphine)dimethylpalladium(II) (deuterated 5, 11, 21, 57, 58) [16]

13. k_2 ($M^{-1}s^{-1}$) at 293 K of reaction with methyl iodide + *cis-bis*(diphenylmethylphosphine)dimethylpalladium(II) (deuterated 5, 11, 21, 47, 57, 58) [16]

14. k_2 ($M^{-1}s^{-1}$) at 403.2 K of substitution between trimethylphenoxytin and methylsulphonyl chloride giving trimethyltin chloride (11, 17, 39, 42, 54) [17]

Reactions of nickel complexes:

15. k_f ($M^{-1}s^{-1}$) at 298.2 K of formation (solvated) nickel(II)-2,2'-bipyridyl complex (3, 4, 5, 10, 11, 13, 16, 17, 18, 19, 22, 23, 24, 26, 27, 29, 31, 32, 34) [18]

16., 17. k_f ($M^{-1}s^{-1}$) and k_d (s^{-1}) at 293.2 K of formation and destruction of (solvated) nickel(II)-thiocyanate monocomplex, respectively (3, 5, 10, 11, 13) [19]

18. k_f ($M^{-1}s^{-1}$) at 298.2 K of formation (solvated) nickel(II)-isoquinoline monocomplex (3, 10, 11, 13, 16) [20]

Reactions with porphyrins:

19. ΔG^\ddagger ($kcal\ mol^{-1}$) at 313.2 K of formation of copper(II)-tetraphenylporphine complex (5, 10, 14, 40, cyclohexanone, propanoic acid) [21]

20. k_f ($M^{-1}s^{-1}$) at 298.2 K of formation of copper(II)-chlorophyll complex (10, 13, 16, 21, 31, 33, 38, 43, 44, 60) [22]

21., 22. k_f ($M^{-1}s^{-1}$) at 298.2 K of formation of cadmium(II)-tetraphenylporphine and cadmium(II)-tetramethoxytetraphenylporphine complex, respectively (16, 23, 27, 31, 32, 36) [22]

Reactions with complexes of platinum group metals:

23. k_{py} (s^{-1}) at 298.2 K hexabromodiplatinic acid dianion reactions with pyridine (4, 9, 10, 11, 12, 15, 18, 21, 25, 28, 44) [9]

24. k_2 ($M^{-1}s^{-1}$) at 298.2 K of carbonyl substitution in (η^5 -nitrocyclopentadienyl)(dicarbonyl)rhodium(I) with triphenylphosphine (11, 13, 39, 40, 57, 61, 65) [23]

25.-30. k_1 (s^{-1}) at 303.2 K of ring closure nucleophilic substitution *mer*-(Rh(III)L(L')Cl₂X)¹⁻ⁿ into *trans*-(Rh(III)L₂Cl₂)⁺+Xⁿ⁻, where Xⁿ⁻ = (pyridine+ClO₄⁻), N₃⁻, SCN⁻, SeCN⁻, or NO₂⁻ and backward (ring opening) reaction where Xⁿ⁻ = NO₂⁻, respectively, L and L' = (*o*-dimethylamino-phenyl)dimethylarsine, -NAs and -As, respectively (13, 16, 23, 24, 30, 34), (8, 13, 16, 23, 30), (8, 13, 16, 23, 24, 30), (8, 13, 16, 23, 30), (13, 16, 23, 24, 30), (13, 16, 23, 24, 30), respectively [11]

Miscellaneous:

31. k_1 (s^{-1}) at 298.2 K intramolecular isomerization of pentaamminenitrito-cobalt(II) into pentaamminenitrocobalt(II) (1, 2, 3, 5, 6, 7, 10, 11, 13, 16, 20, 21, 33, 40, 41, 44) [10]

32., 33. k_f ($M^{-1}s^{-1}$) and k_d (s^{-1}) at 298.2 K of Na(I) and 4,7,13-trioxo-1,10-diazabicyclo[8,5,5]eicosane complex (4, 10, 11, 13, 21, 33) [24]

34. r as relative rate of reaction of N-phenylethanamide with sodium (40, 41, 49, 51, 56, 57, 58, 61) [25]

35. k_2 ($M^{-1}s^{-1}$) at 298.2 K of ring closure reaction of (1,10-phenanthroline)(pentacarbonyl)molybdenum complex (40, 45, 46, 57, 58) [26]

36., 37. k_2 ($M^{-1}s^{-1}$) at 298.2 K of substitution of solvent in (solvent)(pentacarbonyl)chromium complex by 1-hexene and piperidine, respectively (45, 46, 57, 58, 64) [27]

38. k_2 ($M^{-1}s^{-1}$) at 298 K of substitution of solvent in (solvent)(η^6 -benzene)(dicarbonyl)chromium complex by carbon monoxide (61, 62, 63, 64, 66) [28]

39. k_2 ($M^{-1}s^{-1}$) at 303 K of oxidation of ethanol to ethanal by pyridinium bromochromate (5, 10, 12, 21, 25, 28, 34, 35, 39, 40, 41, 43, 44, 48, 55, 57, 58, 60, 61) [8]

Table 1

Values of squared Hildebrand's parameter, δ^2_H ; polarizability, P ; deprotonation enthalpy, DPE; and proton affinity, PA, of the solvents represented in reactions considered in this work. Solvents are given in the order of descending value of Kirkwood function

No.	Solvent	δ^2_H	P	DPE	PA
1	N-MeF	951.8	0.2059	360.4	207.6
2	Formamide	1499.0	0.2109	359.9	202.6
3	H ₂ O	2408.4	0.1706	390.8	166.5
4	Propylene carbonate	762.7	0.2016		
5	DMSO	600.0	0.2009	366.6	213.9
6	1,2,3-P.(OH) ₃		0.2196		
7	Sulpholane	751.0	0.2222		
8	1,2-Et(OH) ₂	887.0	0.2059		
9	DMA	533.9	0.2079	374.9	219.4
10	DMF	598.1	0.2055	399.0	214.2
11	MeCN	619.3	0.1749	372.9	191.5
12	PhNO ₂	532.2	0.2433	354.2	193.4
13	MeOH	910.2	0.1690	379.2	185.6
14	HMPT		0.2143		227.4
15	EtCN	503.2	0.1828	375.0	194.1
16	EtOH	715.1	0.1812	376.1	190.4
17	PhCN		0.2357	383.2	199.5
18	PrCN	445.0	0.1896		195.4
19	Acrylonitrile		0.1920	371.2	189.7
20	AcOAc		0.1917		
21	Me ₂ CO	413.6	0.1804	368.8	198.5
22	Me ₃ PO ₄		0.1940		212.0
23	PrOH	626.6	0.1899	374.7	192.6

Table 1 continued

No.	Solvent	δ^2_{H}	P	DPE	PA
24	<i>i</i> PrOH	585.6	0.1872	374.1	194.2
25	EtMeCO	382.1	0.1876	370.2	201.4
26	<i>i</i> BuOH	534.5	0.1936	374.7	192.4
27	BuOH	565.6	0.1949	373.7	193.2
28	PhMeCO		0.2380	362.4	207.9
29	<i>s</i> BuOH	543.5	0.1944	372.9	195.0
30	2-(MeO)-EtOH	565.2	0.1960	373.8	
31	PnOH	521.4	0.1986	373.9	
32	HexOH	370.0	0.2012	372.2	
33	Pyridine	491.9	0.2301	391.9	223.9
34	<i>i</i> BuOH	490.6	0.1908	373.3	198.8
35	1,2-EtCl ₂	431.6	0.2101		
36	OctOH	446.6	0.2051	372.0	
37	1,2-PhCl ₂	440.9	0.2420		
38	Quinoline	453.1	0.2616	384.3	227.6
39	MeCl ₂	441.1	0.2034	374.6	
40	THF	387.3	0.1969		200.8
41	Monoglyme	345.1	0.1879		204.9
42	MeBr ₂	522.7	0.2394		
43	AcOH	398.0	0.1852	351.9	191.8
44	EtOAc	357.8	0.1853		202.6
45	PhCl	396.8	0.2343	387.2	184.6
46	PhF	361.7	0.2176	393.9	185.0
47	PhNMe ₂	397.2	0.2439		226.0
48	CHCl ₃	381.4	0.2105	357.1	
49	PhOMe	425.8	0.2323		203.9
50	Et ₂ O	237.1	0.178		201.9
51	PhOEt	384.0	0.2296		
52	<i>i</i> Pr ₂ O	210.0	0.1837		207.8
53	Bu ₂ O	250.7	0.1948		203.7
54	MeOMeOMe		0.1776		
55	CS ₂	446.0	0.2623		164.4
56	1,2-PhMe ₂	355.2	0.2277		195.9
57	PhMe	352.1	0.2261	380.8	192.6
58	PhH	373.1	0.2276	400.7	184.8
59	CCl ₄	330.0	0.2150		
60	Dioxane	446.0	0.2028		195.3
61	<i>c</i> -Hexane	300.0	0.2042	403.7	169.0
62	Dodecane	267.8	0.2025		
63	Decane	260.6	0.1986		
64	Heptane	245.6	0.1908		
65	Hexane	235.4	0.1862		
66	Pentane	224.3	0.1799		

RESULTS AND DISCUSSION

Solvent parameters

Correlations between parameters (Table 2) are comparable with those [4] with a different set of solvents. Universal parameters Y and $E_T(30)$ correlate with almost all other parameters. Acidity parameters, except deprotonation enthalpy (DPE), are mutually highly correlated, similarly to basicity parameters. Polarity parameters μ and π^* tend to correlate with basicity, while P and δ_H^2 tend to correlate with acidity parameters. The most optimal single polarity parameter seems to be γ , independent of AN and DN, proton affinity (PA) and DPE, α and β . The rest of acidity parameters (E , AN, α) do not correlate with DPE. Correlations of dipole moment with both DPE and PA may be meaningful because all three parameters are measured in the gas phase. The extended parameter DN (with more values for HBD solvents) correlates with certain acidity and polarity parameters. Negligible correlations between λ and all other parameters, except those expressing basicity, may need attention. However, the number of known values is insufficient, and the parameter is expressed in nm, not in cm^{-1} , which would be proportional to the energy unit. Reflection of interactions on parameters does not depend on the exact definition and critical evaluation of the model process only. Relations between the nature of each single solvent and parameter values for it are much more complicated. The basic properties of a protic (HBD) solvent are evidently influenced by the strength of hydrogen bonds and vice versa, so that correlations between basicity and acidity parameters are probably not absolutely accidental or caused because parameters describe electrostatic interactions partially. Values of empirical parameters are often unknown for experimental reasons (e.g., low solubility of a model compound in a respective solvent) or affected by steric hindrances and secondary processes. However, it is particularly hard to set a border between polarity and acidity parameters. Some values of polarity parameters indicate the influence of hydrogen bonds and other specific interactions. Some comparable values of acidity parameters for less polar acidic solvents and polar solvents without considerable acidic properties cannot be interpreted in terms of specific interactions. Some values of acidity parameters for C-H acids (e.g. ketones) seem to be underestimated.

Selection of parameters for a multiparameter equation

To describe possibly more data of very different reactions there is no need to search for similar processes (which is often useful in the case of a single reaction) or universal parameters expressing the share of all possible interactions (which is optimal when describing processes by a single parameter), but it is essential to find fundamental orthogonal parameters, each expressing a single physical or chemical interaction. Correlations between parameters depend on the set of solvents. However, it seems (see Table 2) that interdependence of many

Table 2

Correlation coefficients between the most important acidity, polarity, and basicity parameters

	n^a	DPE ^b	α^c	AN ^d	E^e	$A(^{14}\text{N})^f$	$E_T(30)^g$	$\delta_{\text{H}}^{\text{h}}$	γ^i	P^j	Y^k	π^{LC}	μ^l	PA ^m	B ⁿ	DS ^o	DN ^p	β^c	λ^q	
DPE	36	-																		
α	47	-0.36	-																	
AN	33		0.95	-																
E	65		0.93	0.94	-															
$A(^{14}\text{N})$	25		0.90	0.96	0.93	-														
$E_T(30)$	65	-0.36	0.82	0.92	0.91	0.93	-													
δ_{H}	58		0.61	0.66	0.74	0.89	0.75	-												
γ	49		<u>0.36</u>	<u>0.33</u>	<u>0.33</u>	<u>0.60</u>	<u>0.43</u>	<u>0.77</u>	-											
P	66		-0.44	-0.35	-0.38		-0.27		0.37	-										
Y	65	0.45	0.37	0.47	0.48	0.55	0.79	0.51	0.37		-									
π^*	50					0.43	0.52	0.51	0.75	0.40	0.74	-								
μ	63	-0.38					0.49	0.38	0.40		0.82	0.69	-							
PA	44		-0.58	-0.44	-0.34	-0.58					0.31	0.35	0.45	-						
B	57						0.36				0.54	0.37	0.49	0.84	-					
DS	45				<u>0.28</u>		0.50	0.36	0.36		0.64	0.49	0.52	0.68	0.93	-				
DN	56		<u>0.28</u>	<u>0.31</u>	0.38		0.51	0.35			0.58	0.35	0.47	0.65	0.85	0.79	-			
β	43		<u>0.31</u>		<u>0.26</u>		0.45				0.60		0.48	0.54	0.81	0.75	0.92	-		
λ	22				<u>0.36</u>									<u>0.41</u>	<u>0.89</u>	<u>0.86</u>	<u>0.85</u>	0.75	-	

^a Number of parameter values for solvents in Table 1. ^b Enthalpy of deprotonation in gas phase (kcal mol⁻¹) [29-32]. ^c Taken from [3]. ^d Taken from [1]. ^e Taken from [33] or calculated $E = E_T(30) - 25.10 - 14.84(\epsilon - 1)/(\epsilon + 2) - 9.59(n^2 - 1)/(n^2 + 2)$. ^f $A(^{14}\text{N})$ of EPR of 2,2,6,6-tetramethylpiperidine N-oxide (mT) [34]. ^g Taken from [1, 35]. ^h Cohesive pressure (MPa) at 298 K, calculated from $(\Delta H_{\text{vap}} - RT)/M$ [36] or taken from [37]. ⁱ Surface tension (mN/m) at 298 K [36]. ^j $(n^2 - 1)/(2n^2 + 1)$ [36]. ^k $(\epsilon - 1)/(2\epsilon + 1)$ [36]. ^l Dipole moment in gas phase (D) [36]. ^m Proton affinity in gas phase (kcal mol⁻¹) [29, 30, 38]. ⁿ ΔV_{OH} of phenol with donor in CCl₄ (cm⁻¹) [39]. ^o ΔV_{sym} of HgBr₂ ref. gas phase (cm⁻¹) [40]. ^p Non-calorimetric values included [41]. ^q λ UV/Vis maxima of Cu(timen)(acac) (nm) [40]. Coefficients with 0.05 < p < 0.1 according to Student's t -test are underlined, with $p > 0.1$ not shown.

parameters of very different character is not accidental, but associated with the intricacy of interactions in the liquid phase and, consequently, with the impossibility to obtain an absolutely clear interpretation for the parameters. Also, correlations may reveal seeming independence of some parameters, because the parameters were measured in a limited group of solvents only.

To obtain specific parameters free from the influence of electrostatic interactions and solvent association, some of them are derived from model processes in inert media, not in bulk solvents. The most inert medium is the gas phase. Thus, it seemed reasonable to take the next step and use specific parameters in a multiparameter equation, measured in the gas phase. Gas-phase acidity (DPE) and gas-phase basicity (PA), though believed to be affected by molecular polarizability, express the most intrinsic acidic and basic properties. Nowadays, a number of their values are available with a sufficient precision. The properties of solvent molecule in the liquid phase, which are different from those in the gas phase, can be expressed by two polarity parameters, δ^2_{H} and P . All four parameters are mutually independent. Thus, the new equation is

$$A = A_0 + h\delta^2_{\text{H}} + pP + a\text{DPE} + b\text{PA}.$$

The coefficients for DPE (a) and PA (b) describe the sensitivity of the reaction to solvent acidity and basicity, the specific properties of a single molecule, if it is not influenced by other molecules. The coefficient for P (p) describes the sensitivity of the reaction to solvent polarizability, the nonspecific property of a bulk solvent, expressing mainly short-distance electrostatic interactions. The coefficient for δ^2_{H} (h) describes the sensitivity of the reaction to the mean liquid-phase polarity, mainly of nonspecific character, as well as the influence of other solvent molecules on the specific properties of a solvent molecule.

Evaluation of the validity of the new multiparameter equation

Correlations between kinetic data and three multiparameter equations were compared (see Table 3) in order to obtain a more adequate picture. For Kamlet-Taft's equation, only four parameters were included; however, the independence of cohesive pressure and other parameters may seem doubtful. For Koppel-Palm's equation, the functions for calculating Y and P are slightly different from those commonly used in original work. The E values used here are taken mainly from reference [33], the others are calculated directly from $E_{\text{T}}(30) - 25.10 - 14.84(\epsilon - 1)/(\epsilon + 2) - 9.59(n^2 - 1)/(n^2 + 2)$. Also, B from the ir stretching frequencies of phenol (not MeOD) was used, since it seemed to be a better selection for obtaining more experimental values for HBD solvents.

Relatively weak correlations between the new equation and data from reactions 14, 15, 20, 23–30, 34, and 39 were evidently caused by the absence of

PA values. Correlations with other multiparameter equations confirmed this supposition. Unknown DPE values seemed to cause weaker correlations with data from reactions 15, 27, and 28. This suggests that the main reason for inadequate results was the absence of parameter values. In most other cases, the importance of a (basic or acidic) specific interaction, suggested by other equations, was confirmed also by the new equation. No comparison revealed the preference of traditional acidity parameters over DPE. For reactions 10, 11, 13, 35, and 38 all three multiparameter equations suggest a similar mechanism.

The results of the correlations are not purely formal. Influences of the basicity, acidity, and polarity of the solvent, suggested by the significance of a respective parameter, are generally consistent with mechanisms proposed by authors of original works. Negative b for reactions 16, 18, 20, 35, and 37 reflects decreasing, and positive b for 17 and 33 increasing nucleophilic solvation in the transition state relative to the ground state. In reactions 4–9, the estimation of highly polar activated complex $R_4M^+I_2^-$ is supported by positive h . In reaction 14, a slightly polar four-centre transition state is proposed, which is in accordance with positive p . In reaction 23, the polar solvent is supposed to accelerate the cleavage and the nucleophilic solvent to compete with pyridine, consistent with positive h and negative b . In reaction 31, electrophilic solvation of the nitrito group, nucleophilic solvation of the amines, and general stabilization of charge-separated transition state are supposed to accelerate the intramolecular isomerization, which is consistent with positive a , b , and h . Both the cation-solvating power and the polarity of the solvent are supposed to support the mechanism of hydride-ion transfer via planar, cyclic, and symmetrical transition state for the decomposition of the ester intermediate in reaction 39, which is in agreement with positive b and h .

The results of correlation of the equation suggested in this work contradict the estimated mechanism of reaction 2, where nucleophilic solvation of the metal centre is supposed to stabilize cyclohexylmercury perchlorate. In reaction 10, where nucleophilic solvation of the associate is supposed to decrease the rate, and in reaction 34, where nucleophilic assistance in polarizing the N–H bond (as a rate limiting step) is considered essential, correlations with all three multiparameter equations indicate the opposite.

The fact that the new multiparameter equation seemed to describe a number of reactions at metal centres satisfactorily, is encouraging. Nevertheless, the general validity of this model is disputable, because more correlations with different data are needed to prove it. Especially crucial is the question whether this equation can describe the processes associated with solvent hydrogen bond donicity. The application area is limited because of the absence of PA and DPE values for certain solvents like aliphatic hydrocarbons and their halogen derivatives, propylene carbonate and sulfolane, and DPE values for ethers and esters.

Correlations between kinetic data ($\ln k$ or ΔG^\ddagger) for reactions considered and multiparameter equations

No.*	A_0	$10^3 h$	p	$10^2 a$	$10^2 b$	R^2 ^a	s^b	ΔA^c	n^d	Lacking value ^e	Kamlet et al. ^f	Koppel-Palm ^f
1		-16.1±3.3	30.3±5.3			0.9100	0.480	3.180	7	54	$A_0, -\beta, -\delta^2_H$	-
2		7.8±2.2		-20.9±5.5	37±10	0.9319	0.855	4.104	6	60	$A_0, -\beta, -\delta^2_H$	$A_0, -Y, -E, -B$
3	-5.59±0.52		-111.2±2.2	2.65±0.26	7.62±0.26	0.9986	0.0331	2.387	6		$-A_0, -\beta, \delta^2_H$	$-A_0, Y, E, -B$
4		19.4±3.5	-68.1±9.6			0.9419	1.330	10.520	5		-	$Y, -P$
5		<u>10.8±5.0*</u>	-54±14			0.9096	1.870	7.639	5		$-A_0, -\beta, \delta^2_H$	-
6		14.7±4.4	-55±12			0.8823	1.661	8.821	5		-	$-A_0, Y, P, -B$
7		15.1±4.6	-56±13			0.8734	1.736	9.268	5		-	$-A_0, Y, P, -B$
8		16.8±3.8	-58±11			0.9068	1.661	9.395	5		$-A_0, \delta^2_H$	$-A_0, Y$
9		16.4±3.8	-56±11			0.8976	1.736	9.115	5		$-A_0, \delta^2_H$	-
10				<u>-2.9±1.0</u>	15.1±1.9	0.9998	0.347	3.300	5		$A_0, -\alpha, \beta$	$Y, -E, B$
11	-7.9±1.3	21.8±3.3				0.9149	0.255	1.952	5		$-A_0, \pi^*$	Y
12			22.0±6.2		-6.26±0.64	0.9477	0.373	1.015	5		$-A_0, -\alpha, -\pi^*, \delta^2_H$	$-A_0, -Y$
13		14.8±2.7		-4.00±0.34		0.9931	0.772	5.154	6		$-A_0, \delta^2_H$	$-A_0, Y, P, E$
14			36.0±2.4			0.9830	1.140	3.450	5		$\beta, -\delta^2_H$	$-Y, -P, B$
15			47.3±3.2			<u>0.9250</u>	2.677	10.120	19		$A_0, -\alpha, -\pi^*, \delta^2_H$	P
16	7.67±2.1	-0.903±0.017		1.491±0.056	-0.609±0.062	0.9995	0.0129	1.466	5		$A_0, -\alpha, -\pi^*$	$A_0, -Y, -E$
17	-32.12±0.91	7.947±0.074		-5.31±0.24	93.03±0.27	0.9997	0.0557	7.313	5		$-A_0, \beta, \pi^*, \delta^2_H$	A_0, Y
18	57.6±1.2		404.2±5.6	-19.65±0.39	-25.30±0.39	0.9993	0.0437	4.332	5		$-A_0, \beta, \pi^*, \delta^2_H$	P
19	-38.3±7.2		27.3±3.4			0.9261	0.875	<u>9.100</u>	6		A_0, β	P, B
20	42.4±4.9		-12.0±1.5	-5.0±1.6		0.9673	0.478	6.356	7	31, 44, 60	$\alpha, -\pi^*$	$E, -B$
21		11.8±1.2		-2.05±0.18		0.9761	0.258	2.884	6		$-A_0, \delta^2_H$	$-P, B$
22		18.07±0.63		-2.59±0.10		0.9944	0.138	4.710	6		$-A_0, \delta^2_H$	$-P, Y$

Table 3 continued

No.*	A_0	$10^3 h$	p	$10^2 \alpha$	$10^2 b$	R^2 ^a	s^b	ΔA^c	n^d	Lacking value ^e	Kamlet et al. ^f	Koppel-Palm ^f
23		3.9±1.2			-2.07±0.28	0.9854	0.297	1.562	8	4, 17, 28	$-A_0, \alpha, -\beta, \pi^*$	$-P, -B$
24	131.8±4.1			-21.56±0.68	-25.66±0.84	0.9971	0.0533	2.111	4	40, 65	δ^2_H	$A_0, -P, -B$
25				-2.066±0.018		0.9996	0.165	0.364	6		$-\beta, -\pi^*$	$-Y, -P, E, B$
26	-16.5±1.7	9.5±2.2				0.8201	0.666	3.991	5		$-\beta$	$Y, -B$
27	-573±114		202±60	1.41±0.28		0.9331	0.328	3.477	5	8	$-\beta$	$-A_0, Y, P, E$
28	-14.3±2.0	8.6±2.7				0.6981	0.823	3.660	5		$-\alpha, -\beta, \delta^2_H$	$E, -B$
29		10.4±2.1		-3.84±0.38		0.9955	0.558	3.938	5		$-\beta, \delta^2_H$	$-P, E$
30			7.3±1.4			0.8681	0.585	1.609	5		$-A_0, \beta, \pi^*$	$P, -E$
31	-16.7±4.2	3.50±0.44	-50±20	-2.53±0.67	13.1±3.2	0.9514	0.268	3.139	10	6, 7, 21, 40, 41, 44	$-A_0, \alpha, \pi^*$	$-A_0, P, E$
32	-23.16±0.47	-6.234±0.087	-129.4±1.0	17.63±0.17		0.9998	0.0205	1.378	5	4	π^*	Y
33					3.29±0.54	0.9039	2.440	5.828	5	4	β	Y
34	15.90±0.51		-69.8±2.4			0.9921	0.1089	2.936	8		$A_0, -\beta, \pi^*$	$A_0, -P$
35			187±37		-18.0±4.4	0.9672	1.620	9.422	5		$A_0, -\beta$	$A_0, -B$
36	54.8±3.9		-201±18			0.9699	0.597	8.276	5		$-\beta, -\pi^*, \delta^2_H$	$A_0, -P$
37	76.3±2.6		-159.4±6.3		-15.7±1.1	0.9963	0.0741	7.797	4	64	$-\pi^*, \delta^2_H$	$A_0, -P$
38		1.69±0.33	36.5±2.2			0.9919	0.0707	1.244	5		$-\delta^2_H$	$-P$
39	-15.8±1.4	4.9±1.3			3.31±0.81	0.8091	0.371	3.507	15	28, 35, 39, 48	$-A_0, \pi^*$	P

* Numbers refer to the reactions characterized on pp. 80-82. ^a R^2 is the square of the adjusted (for degrees of freedom) correlation coefficient, underlined if Durbin-Watson characteristic is less than 1.5, and thus residuals tend to change monotonously by changing a dependent parameter, indicating a poor parameter selection. ^b Standard error of estimation. ^c $A_{max} - A_{min}$, underlined when maximum or minimum rate logarithm in the original paper is for a solvent in case of which the value of parameter(s) giving the best correlation is unknown. ^d Number of solvents giving the best correlation here, underlined when the actual number in the original work is bigger. All solvents for which parameter values are known are included. ^e Numbers of solvents (in Table 1) for which the parameter value is unknown. ^f Parameters of other multiparameter equations, by Kamlet et al. (four parameters only) and by Koppel and Palm (definitions of parameters in Table 2), respectively, given in bold when describing the data better than this equation, parameter underlined if $p > 0.05$. ^g Constants and coefficients of parameters are underlined, if $p > 0.05$ and thus the necessity to use this parameter is not proved, however, the choice including the parameter seems to be the best with this set of parameters.

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REFERENCES

1. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*. VCH, Weinheim, 1990.
2. Koppel, I. A. & Palm, V. A. The influence of the reagent on organic reactivity. In *Advances in Linear Free Energy Relationships* (Chapman, N. B., Shorter, J., eds.), Ch. 5. Plenum, London, 1972, 203–280.
3. Kamlet, M. J., Abboud, J.-L. M., Abraham, M. H. & Taft, R. W. Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters, π^* , α , and β , and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.*, 1983, **48**, 17, 2877–2887.
4. Pytela, O. Empirical approach to description of solvent effect on processes in solutions: A review. *Collect. Czech. Chem. Commun.*, 1988, **53**, 7, 1333–1423.
5. Palm, V. A. & Palm, N. V. On the total number and list of parameter scales significant for general quantitative description of solvent effects. *Organic Reactivity* (Tartu), 1993, **28**, 1, 125–150.
6. Maria, P.-C., Gal, J.-F., Franceschi, J. de & Fargin, E. Chemometrics of the solvent basicity: Scales relevant to non-protogenic solvents. *J. Am. Chem. Soc.*, 1987, **109**, 2, 483–492.
7. Petrosyan, V. S. Solvent effects on the rates and mechanisms of organotin alkyl exchange reactions. *J. Organomet. Chem.*, 1983, **250**, 1, 157–170.
8. Aparna, P., Kothari, S. & Banerji, K. K. Kinetics and mechanism of the oxidation of primary aliphatic alcohols by pyridinium bromochromate. *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1995, **107**, 3, 213–220.
9. Kolling, O. W. Solvent effects on the kinetics of cleavage of bromo-bridged platinum(II) complexes. *J. Phys. Chem.*, 1987, **91**, 16, 4388–4390.
10. Jackson, W. G., Lawrance, G. A., Lay, P. A. & Sargeson, A. M. Solvent dependence, metal ion catalysis and base catalysis of nitrito to nitro linkage isomerization of pentaamminenitrocobalt(II). *Austral. J. Chem.*, 1982, **35**, 8, 1561–1580.
11. Peloso, A. Solvent effects on rates and equilibria of chelate ring-closure ring-opening nucleophilic substitution reactions of octahedral rhodium(III) complexes. *J. Chem. Soc. Dalton Trans.*, 1982, 11, 2141–2146.
12. Tuulmets, A. Effect of solvents on Grignard reaction. XIII. A quantitative treatment of the medium effects. *Organic Reactivity* (Tartu), 1974, **11**, 1, 81–100.
13. Reutov, O. A., Beletskaya, I. P. & Sokolov, V. I. *Mekhanizmy Reaktsii Metalloorganicheskikh Soedinenii*. Khimiya, Moscow, 1972 (in Russian).
14. Fukuzumi, S. & Kochi, J. K. Electron donor-acceptor complexes. 2. Quantitative evaluation of solvent effects on the reactivity of alkylmetals. *J. Phys. Chem.*, 1980, **84**, 18, 2254–2261.
15. Korinets, E. D., Fedorov, L. A., Rokhlin, E. M., Kravtsov, D. N. & Fedin, E. I. Issledovanie reaktsii obmena mezhdru khloridom i metilmerkaptidom trimetilolova v inertnykh rastvorityakh metodom PMR. *Izv. Akad. Nauk. Ser. Khim.*, 1978, 5, 1182–1184 (in Russian).

16. Moravskiy, A. & Stille, J. K. Mechanisms of 1,1-reductive elimination from palladium: Elimination of ethane from dimethylpalladium(II) and trimethylpalladium(IV). *J. Am. Chem. Soc.*, 1981, **103**, 14, 4182–4186.
17. Kozuka, S., Yamaguchi, S. & Tagaki, W. The mechanism of the reaction of (aryloxy)trimethylstannane with methanesulfonyl chloride. Solvent and substituent effect on the rate of the reaction. *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2, 573–576.
18. Munakata, M., Kitagawa, S. & Miyazima, M. Classification of solvents based on their coordination power to nickel(II) ion. A new measure for solvent donor ability. *Inorg. Chem.*, 1985, **24**, 11, 1638–1643.
19. Dickert, F., Hoffmann, H. & Janjic, T. Mechanism of complex formation in polar solvents. Relation between rates of formation and dissociation and the donicity of the solvent. *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 7, 712–718.
20. Ishihara, K., Fumahashi, S. & Tanaka, M. Activation volume as evidence for a dissociative-interchange mechanism of nickel(II) ion complexation with isoquinoline in water, N,N-dimethylformamide, acetonitrile, methanol, and ethanol. *Inorg. Chem.*, 1983, **22**, 18, 2564–2567.
21. Longo, F. R., Brown, E. M. & Quimby, D. J. Kinetic study on metal chelation by porphyrins. *Ann. New York Acad. Sci.*, 1973, **206**, 420–442.
22. Berezin, B. D. & Krestov, G. A. Kompleksoobrazovanie i sol'vatatsiya porfirinov v rastvorakh. In *Kompleksoobrazovanie v nevodnykh sredakh* (Krestov, G. A., ed.), Ch. 6. Nauka, Moscow, 1994, 190–223 (in Russian).
23. Rerek, M. E. & Basolo, F. Kinetics and mechanism of substitution reactions of η^5 -cyclopentadienyldicarbonylrhodium(I) derivatives. Rate enhancement of associative substitution in cyclopentadienylmetal compounds. *J. Am. Chem. Soc.*, 1984, **106**, 20, 5908–5912.
24. Lincoln, S. F., Brereton, I. M. & Spotswood, Th. M. The complexation of sodium ion by the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]icosane (C21C5) in a range of solvents. A ^{23}Na nuclear magnetic resonance kinetic study. *J. Am. Chem. Soc.*, 1986, **108**, 26, 8134–8138.
25. Golovin, M. V. *Sintez i reaktsii na osnove metallirovannykh anilidov*. Ufa, 1975 (in Russian).
26. Cao, S., Shi, Y., Hollmann, J., van Eldik, R. & Eyring, E. M. Mechanism of chelation of phenanthroline derivatives to $\text{Mo}(\text{CO})_5$ deduced from pulsed photolysis studies in several solvents at high pressure. *J. Chem. Soc. Dalton Trans.*, 1996, **8**, 1629–1635.
27. Zhang, S., Zang, V., Bajaj, H. C., Dobson, G. R. & van Eldik, R. Octahedral metal carbonyls. LXXII. Volumes of activation for solvent displacement in (solvent) $\text{M}(\text{CO})_5$ transients ($\text{M}=\text{Cr}, \text{Mo}, \text{W}$) generated from $\text{M}(\text{CO})_6$ via pulsed laser flash photolysis. *J. Organomet. Chem.*, 1990, **397**, 279–289.
28. Creaven, B. S., George, M. V., Ginzburg, A. G., Hughes, C., Kelly, J. M., Long, C., McGrath, I. & Pryce, M. T. Laser pulse photolysis transient infrared investigation into effect of solvent or substituents (X) on the reactivity of photogenerated ($\eta^6\text{-C}_6\text{H}_6\text{-yXy}$) $\text{Cr}(\text{CO})_2$ intermediates. *Organometallics*, 1993, **12**, 8, 3127–3131.
29. Koppel, I. A., Mölder, U. H., Pikver, R. I., Mazunov, V. A. & Khvostenko, V. I. *Elektronnoe i protonnoe srodstvo molekul*. BNTs UrO AN, Ufa, 1991 (in Russian).
30. Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D. & Mallard, W. G. Gas-phase ion and neutral thermochemistry. *J. Phys. Chem. Ref. Data*, 1988, **17**, Suppl. 1.
31. Burk, P. & Koppel, I. A. Critical test of PM3 calculated gas-phase acidities. *Theor. Chim. Acta*, 1993, **86**, 417–427.
32. Meot-Ner, M. & Kafafi, S. A. Carbon acidities of aromatic compounds. *J. Am. Chem. Soc.*, 1988, **110**, 19, 6297–6303.
33. Koppel, I. A. & Paju, A. I. Extended scale of solvent electrophilicity. *Organic Reactivity* (Tartu), 1974, **11**, 1, 137–140.

34. Kecki, Z., Liczkowski, B. & Kolodziejski, W. Critical comparison of empirical systems used to describe solvent properties. *J. Solut. Chem.*, 1986, **15**, 5, 413–422.
35. Reichardt, C. & Schaefer, G. Determination of new and corrections of old $E_T(30)$ values as empirical measures of solvent polarity for 40 organic solvents. *Liebigs Ann. Chem.*, 1995, **8**, 1579–1582.
36. *CRC Handbook of Chemistry and Physics* (Lide, D. R., ed.), 75th edition. CRC Press, Boca Raton, 1994.
37. Dack, M. R. The importance of solvent internal pressure and cohesion to solution phenomena. *Chem. Soc. Rev.*, 1975, **4**, 211–229.
38. Burk, P., Herodes, K., Koppel, I. & Koppel, I. A. Critical test of PM3-calculated proton affinities. *Intern. J. Quantum Chem.*, 1993, **27**, 633–641.
39. Koppel, I. A. & Paju, A. I. Parameters of general basicity of solvents. *Organic Reactivity* (Tartu), 1974, **11**, 1, 121–136.
40. Sandström, M., Persson, I. & Persson, P. A study of solvent electron-pair donor ability and Lewis basicity scales. *Acta Chem. Scand.*, 1990, **44**, 7, 653–675.
41. Marcus, Y. The effectivity of solvents as electron pair donors. *J. Solut. Chem.*, 1984, **13**, 9, 599–624.

METALLIÜHENDITE KINEETIKA SOLVENDIEFEKTIDE KVANTITATIIVNE KIRJELDUS NELJAPARAMEETRISE VÖRRANDI ABIL

Aimar KUKK

On arvatud 66 solvendi happelisust, polaarsust ja aluselisust väljendavate parameetrite korrelatsioonid. Mitmeparameetrilise võrrandi tarvis on välja valitud neli omavahel sõltumatut parameetrit: happelisus gaasifaasis (deprotooneerimisentalpia, DPE), aluselisus gaasifaasis (protonafiinsus, PA), polariiseritavus ($P = (n^2 - 1) / (2n^2 + 1)$) ning Hildebrandi parameeter ruudus (δ^2_H). Metallitsentrite juures toimuva 39 reaktsiooni kiiruse logaritmid on korreleeritud saadud võrrandiga ja võrdluseks Koppeli–Palmi võrrandiga ning Kamleti ja kaasautorite võrrandiga. Uus võrrand kirjeldab kineetilisi andmeid enamasti rahuldavalt. Siiski oleks võrrandi üldise kehtivuse tõestamiseks vaja rohkem korrelatsioone erinevate andmetega. Korreleerimistulemusi mõjutas PA ja DPE väärtuste ebapiisav hulk. Traditsioonilise happelisuse parameetri puudumine võrrandist ei põhjustanud nõrgemaid korrelatsioone. On välja pakutud uue võrrandi parameetrite tõlgendusvõimalused.