

QUANTITATIVE DESCRIPTION OF ACIDITY OF XOH COMPOUNDS IN THE GAS PHASE AND DIMETHYL SULPHOXIDE WITH USE OF HOMO ENERGIES OF XO⁻ ANIONS

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An approach to the quantitative evaluation of XOH acidity in the gas phase and in dimethyl sulphoxide solution is described. It is based on one-parameter correlations between the acidities of XOH family members and the electron affinities of the XO[·] radicals or highest occupied molecular orbitals (HOMO) energies of the corresponding XO⁻ anions. The approach is based on Koopmans' theorem and provides familial correlations for the acidities of alcohols, carboxylic acids, phenols and mineral acids with calculated (MNDO, AM1 or PM3) HOMO energies of their anions.

INTRODUCTION

During the last 10-15 years, the dramatic increase in experimental data for OH acidities, both in the gas phase¹⁻⁵ and in dimethyl sulphoxide (DMSO),⁶⁻¹⁴ has given rise to efforts towards their quantitative description. The deprotonation energy (the difference between total energy of XO⁻ anion and that of initial XOH acid) has been used for the quantitative *a priori* estimation of XOH acidity. The calculated deprotonation enthalpies agree fairly well with corresponding experimental values in the gas phase.¹⁵⁻¹⁹ However, the calculations are time consuming and, therefore, justified only for the prediction of acidities that are difficult to determine by direct measurements.¹⁵

Recently, a quantitative description of OH acidity in the gas phase and DMSO of XOH compounds by means of a three-parameter equation, which includes parameters for X-substituent polarizability, inductive/field and resonance effects was proposed.^{2,20,21} Another approach to quantitative estimation of XOH acidity, $\Delta G_{\text{acid}}^0 = \Delta H_{\text{acid}}^0 - T\Delta S_{\text{acid}}^0$ is based on the thermodynamic cycle of a proton transfer reaction:⁴

$$\Delta H_{\text{acid}}^0 = BDE(\text{XO-H}) - EA(\text{XO}^{\cdot}) + IE(\text{H}^{\cdot}) \quad (1)$$

where $BDE(\text{XO-H})$ is the energy of the homolytic dissociation of the OH bond in XOH and $EA(\text{XO}^{\cdot})$ is the electron affinity of the XO[·] radical. Therefore, equation (1) can be applied, with allowance for the constancy of the hydrogen atom ionization energy $IE(\text{H}^{\cdot}) = 313.6 \text{ kcal mol}^{-1}$ (1 kcal = 4.184 kJ) and of the entropy term $T\Delta S_{\text{acid}}^0$, as follows:

$$\Delta G_{\text{acid}}^0 = BDE(\text{XO-H}) - EA(\text{XO}^{\cdot}) + \alpha \quad (2)$$

where

$$\alpha = IE(\text{H}^{\cdot}) - T\Delta S_{\text{acid}}^0 = \text{constant} \quad (3)$$

Equation (2) can be transformed^{20,21} into a one-parameter relationship (5) on assumption of either a proportional change in the dissociation energy of the XO-H bond and the electron affinity of the XO[·] radicals:

$$BDE(\text{XO-H}) = \beta EA(\text{XO}^{\cdot}) + \gamma \quad (4)$$

where β and γ are constants, and/or constant $BDE(\text{XO-H})$ values:

$$\Delta G_{\text{acid}}^0 = aEA(\text{XO}^{\cdot}) + b \quad (5)$$

where the slope $a = \beta - 1$ and intercept $b = \alpha + \gamma$ are constants which are characteristic for a given family of

XOH compounds. In the general case, the coefficient a before $EA(X^\cdot)$ is not expected to be equal to -1 as in equations (1) and (2). One can see that $a = -1$ only on condition that $\beta = 0$ and $BDE(XO-H) = \gamma = \text{constant}$. The dependence of the enthalpy ΔH_{acid}^0 on $EA(XO^\cdot)$ for six aliphatic alcohols has been observed²⁰ over a fairly narrow range of ΔH_{acid}^0 values and attempts to determine the dependence of ΔH_{acid}^0 on $EA(XO^\cdot)$ over a wider

range of ΔH_{acid}^0 for alcohols, phenols, carboxylic and mineral acids have been made.²⁰

RESULTS AND DISCUSSION

This work was aimed at the description of OH acidity in the gas phase and in DMSO in the framework of the one-parameter equation (5). It is based on the large

Table 1. Gas-phase acidity (ΔG_{acid}^0),¹ acidity in DMSO (pK_a)⁶ of OH-acids XOH, homolytic dissociation energy of the XO-H bond (BDE), electron affinity of radicals XO^\cdot (EA)¹ and HOMO energies of XO^\cdot (E_{HOMO}), calculated by the MNDO, AM1 and PM3 methods in this work

No.	Compound XOH	ΔG_{acid}^0 (kcal mol ⁻¹)	pK_a (DMSO)	BDE (kcal mol ⁻¹)	$EA(XO^\cdot)$ (eV)	$-E_{\text{HOMO}}$ (eV)		
						MNDO	AM1	PM3
<i>Alcohols</i>								
1	H ₂ O	384.5	31.4	117.9 ⁵ 119.0 ²²	1.83 ⁵	0.47	0.87	1.01
2	CH ₃ OH	374.4 375.1 ⁵	29.0	104.1 ⁵ 104.4 ²³	1.57 ⁵	2.41	2.05	1.79
3	C ₂ H ₅ OH	371.0 372.0 ⁵	29.8	104.3 ⁵ 103.3 ²³	1.73 ⁵	2.47	2.13	1.92
4	C ₃ H ₇ OH	369.9	—	103.2 ²³	1.79 ⁵	—	2.24	2.03
5	<i>i</i> -C ₃ H ₇ OH	369.1 370.1 ⁵	30.3	104.9 ⁵ 102.7 ²³	1.84 ⁵	—	2.33	2.20
6	<i>t</i> -C ₄ H ₉ OH	368.4 369.3 ⁵	32.2	105.2 ⁵ 102.1 ²³	1.91 ⁵	2.63	2.57	2.54
7	<i>s</i> -C ₄ H ₉ OH	367.9	—	105.5 ²²	1.95	—	2.36	2.14
8	CH ₃ OCH ₂ CH ₂ OH	367.2	—	—	1.90	—	2.47	1.21
9	PhCH ₂ OH	363.6	—	—	2.14	—	2.82	2.59
10	CH ₂ FCH ₂ OH	363.9	—	—	2.10	2.93	2.58	2.40
11	CHF ₂ CH ₂ OH	359.6	—	—	2.23	—	3.06	2.90
12	CF ₃ CH ₂ OH	354.5	23.5	—	2.42	4.20	3.72	3.97
13	CF ₃ CH(CH ₃)OH	353.7	—	—	2.54	—	3.45	3.97
14	CF ₃ CF ₂ CH ₂ OH	349.0	—	—	2.70	—	3.82	4.09
15	CF ₃ OH	341.0 ²	—	—	—	4.95	4.98	5.05
16	(CF ₃) ₂ CHOH	338.5	16.0 ¹⁰	—	3.19	5.51	4.99	4.98
17	(CF ₃) ₃ COH	324.4	10.7	—	3.77	6.57	6.01	5.98
18	CH ₂ =CHOH	350.0 ²	—	—	1.82	1.68	1.91	1.86
<i>Phenols</i>								
19	PhOH	342.6	18.0 ^{7a}	90.0 ²⁴	2.20	2.52 ¹³	2.69 ¹³	2.69
20	4-CH ₃ OC ₆ H ₄ OH	343.8	19.1 ^{7a}	84.6 ^{7a} 78.1 ²⁵	2.15	2.75	2.89	2.84
21	4-CH ₃ C ₆ H ₄ OH	343.4	18.9 ^{7a}	88.7 ^{7a}	2.16	2.67	2.71	2.69
22	4-FC ₆ H ₄ OH	340.2	—	—	2.31	—	2.87	2.92
23	3-FC ₆ H ₄ OH	337.1	15.9 ^{7b}	—	2.45	—	3.05	3.05
24	4-ClC ₆ H ₄ OH	336.6	16.8 ^{7a}	84.4 ²⁵ 90.3 ^{7a}	2.47	—	3.04	2.99
25	3-ClC ₆ H ₄ OH	335.4	15.8 ^{7a}	91.8 ^{7a}	2.52	3.02	3.04	2.99
26	3-CF ₃ C ₆ H ₄ OH	332.8	14.9 ⁸ 15.6 ^{7a}	93.8 ^{7a}	2.64	3.22	3.34	3.31
27	4-CF ₃ C ₆ H ₄ OH	330.4	15.2 ^{7a}	87.2 ²⁵ 95.3 ^{7a}	2.74	—	3.59	3.58
28	3-NO ₂ C ₆ H ₄ OH	327.6	14.4 ^{7a}	94.3 ^{7a}	2.85	2.66	2.79	2.78
29	3,4,5-Cl ₃ C ₆ H ₂ OH	323.9	12.7 ^{7a}	93.1 ^{7a}	3.00	3.81	3.66	3.54
30	3,5-(CF ₃) ₂ C ₆ H ₃ OH	323.2	13.1 ⁹	—	3.05	3.89	3.94	3.90
31	4-NO ₂ C ₆ H ₄ OH	321.3	10.8 ^{7a}	94.7 ^{7a}	3.55 ²⁶	3.86 ¹³	4.14 ¹³	4.24
32	C ₆ F ₅ OH	320.8 ³	8.9 ¹⁴	—	3.06	4.08	3.87	4.00

Table 1. Continued

No.	Compound XOH	ΔG_{acid}^0 (kcal mol ⁻¹)	pK_a (DMSO)	BDE (kcal mol ⁻¹)	$EA(XO')$ (eV)	$-E_{\text{HOMO}}$ (eV)		
						MNDO	AM1	PM3
33	4-CF ₃ SO ₂ C ₆ H ₄ OH	315.7	—	—	3.36	5.34	4.70	4.21
34	2,4,6-(NO ₂) ₃ C ₆ H ₂ OH	302.3	—	—	—	6.00	6.05	6.21
35	2-C ₁₀ H ₇ H	336.8	17.1 ^{7a}	88.0 ^{7a}	—	2.89	3.03	3.02
36	1-C ₁₀ H ₇ OH	—	16.2 ^{7a} 15.4 ¹²	84.0 ^{7a}	—	2.80	2.93	2.93
37	1,4-(NO ₂) ₂ C ₁₀ H ₆ OH	—	8.9 ¹²	—	—	3.94	4.19	—
38	1-OH-antraquinone	—	14.0 ¹³	—	—	3.60	3.84	3.72
39	1-OH-4-NO ₂ -antraquinone	—	10.0 ¹³	—	—	4.61	4.81	4.82
<i>Carboxylic acids</i>								
40	HCOOH	338.4	10.4 ¹⁰	107.7 ²³	3.26	3.74	3.66	3.56
41	CH ₃ COOH	341.5	12.4 ¹⁰	105.7 ²³	3.01	—	3.96	3.93
42	PhCOOH	331.7	11.0 ¹⁰	104.3 ²³	3.39	4.29	4.68	4.46
43	FCH ₂ COOH	331.3	—	—	3.70	—	4.26	4.32
44	ClCH ₂ COOH	328.8	8.9 ¹⁰	—	3.61	—	4.46	4.40
45	F ₂ CHCOOH	323.8	6.2 ¹⁰	—	3.85	—	4.64	4.70
46	NCCH ₂ COOH	323.7	8.2 ¹⁰	—	3.87	4.80	4.92	—
47	Cl ₂ CHCOOH	320.9	6.3 ¹⁰	—	3.96	—	4.91	4.78
48	CF ₃ COOH	316.4	3.6 ¹⁰	112.0 ²³	4.20	—	5.28	5.25
49	C ₆ F ₅ COOH	316.6 ³	—	—	—	4.35	4.67	4.45
50	CCl ₃ COOH	312.8	—	—	—	5.14	5.33	5.07
<i>Mineral acids</i>								
51	HOF	362.0 ²	—	—	2.05	1.60	1.73	2.58
52	HOCl	348.0 ²	—	—	2.17	2.54	2.69	2.50
53	HNO ₂	330.5	7.5	—	2.35	3.06	3.00	2.51
54	HNO ₃	317.8	—	—	3.70	5.41	5.81	5.72
55	CH ₃ SO ₃ H	315.0 ³	1.6	—	—	5.73	6.41	5.45
56	HPO ₃	303.3 ²⁷	—	—	5.20 ²⁷	—	—	—
57	H ₂ SO ₄	302.2 ²⁷	—	103.8 ²⁷	4.50	6.34	7.28	6.00
58	FSO ₃ H	299.8 ²⁷	—	105.0 ²⁷	4.80 ²⁷	6.82	7.24	6.22
59	CF ₃ SO ₃ H	299.0 ²⁷	0.3	—	4.90	6.93	6.33	6.39
60	HClO ₄	285.0	—	—	5.40 ² 5.82	6.83	7.23	—

collection of experimental values of ΔG_{acid}^0 , $pK_a(\text{DMSO})$, $BDE(\text{XO}-\text{H})$ and $EA(\text{XO}')$ that have been obtained to date.

Table 1 presents literature data on the gas-phase acidities (ΔG_{acid}^0), acidities in DMSO (pK_a), dissociation energies of $\text{XO}-\text{H}$ bonds (BDE) and experimental electron affinities of XO' radicals for families of alcohols, phenols, carboxylic and mineral acids. In addition, the HOMO energies of XO' anions calculated in this work by MNDO, AM1 and PM3 methods are given. Selected series of compounds cover the maximum range of acidity: 90 kcal mol⁻¹ in the gas phase and ca 30 pK_a units in DMSO solution.

The BDE values for alcohols ROH and carboxylic acids are known to be centred within the limits of 104 ± 2 kcal mol⁻¹ and 106 ± 2 kcal mol⁻¹, respectively,²² which is consistent with a negligible contribution of resonance to the stabilization of the heteroallyl radical, $\text{O}=\text{C}(\text{R})-\text{O}'$, and also the alkoxy

radical RO' .²⁸ Therefore, the changes in the experimental values of BDE and EA for alcohols and carboxylic acids are symbiotic (Figure 1). The dependence of BDE values on EA for phenols is more sensitive to the phenoxy radical structure (Figure 1).^{7a}

Three separate relationships have been obtained between the gas-phase acidity ΔG_{acid}^0 and $EA(\text{XO}')$ for alcohols and carboxylic acids [Figure 2, line I; equation (1) in Table 2], phenols [Figure 2, line II; equation (2) in Table 2] and mineral acids [Figure 2, line III; equation (3) in Table 2]. It should be emphasized that the point for vinyl alcohol (Table 1, No. 18) fits line II for phenols (Fig. 2) because of the significant resonance effect of the $\text{CH}_2=\text{CH}-\text{O}'$ radical^{7a} and in the $\text{CH}_2=\text{CH}-\text{O}'$ anion.¹⁷ Point No. 1 for H₂O deviates from line I (Figure 2) owing to the extremely high $BDE(\text{HO}-\text{H})$ value and, consequently, the high value of ΔG_{acid}^0 . Points 51 and 52, for HOF and HOCl, deviate from line III (Figure 2) for mineral acids because of

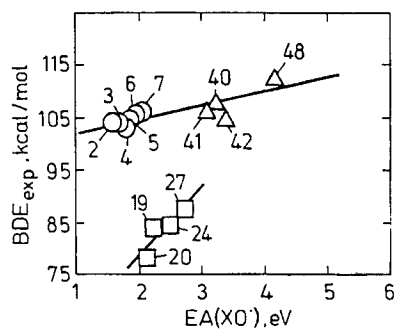


Figure 1. Dependencies of BDE values on the EA(XO[•]) values for the series of compounds: alcohols (O), carboxylic acids (Δ), and phenols (\square). Numbering of points is given according to Table 1

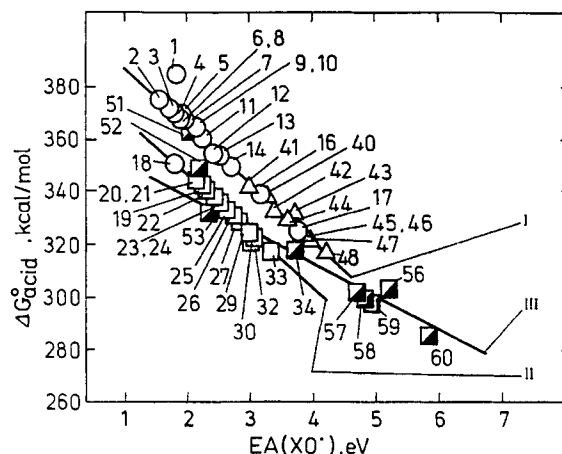


Figure 2. Dependencies of the acidity (ΔG_{acid}^0) values of series of acids XOH in gas phase on the EA values of radicals XO[•] in gas phase (the numbering of points corresponds to the data of Table 1, equations (1)–(3) in Table 2; O, Δ , line I for alcohols and carboxylic acids; \square , line II for phenols; \blacksquare , line III for mineral acids)

anion destabilization which results from the repulsion between lone pairs of electrons on the halogens and those of an anionic centre (α -effect).² Therefore, a quantitative description of the OH acidity of XOH compounds in the gas phase in the framework of the one-parameter dependence of ΔG_{acid}^0 on EA(XO[•]) values proves to be useful, since it divides all XOH com-

Table 2. Correlation equations relating gas-phase acidities ($-\Delta G_{\text{acid}}^0$, kcal mol⁻¹), acidities in DMSO (pK) of acids XOH, electron affinities of XO[•] (EA, eV) and HOMO energies of XO⁻ (E_{HOMO} , eV) calculated by MNDO, AM1 and PM3 methods^a

Parameter	Equation No.	Compound No.	<i>a</i>	<i>b</i>	<i>r</i>	<i>n</i>
$\Delta G_{\text{acid}}^0 = aEA_{\text{exp}}(\text{XO}^\bullet) + b$ (Figure 2)	1	2–14, 16, 17, 40–48	-22.64	410.98	0.998	24
	2	18–30, 32, 33	-23.05	393.17	0.998	15
	3	53, 54, 56–60	-12.5	361.5	0.970	7
$E_{\text{HOMO}} = aE_{\text{HOMO}}(\text{AM1}) + b$	4	1-36, 38–45, 47–55, 57–59 (PM3)	0.91	0.26	0.976	56
	5	1–3, 6, 10, 12, 15–21, 25, 26, 28–40, 42, 46, 49–55, 57–60 (MNDO)	0.96	0.12	0.977	41
$EA_{\text{exp}}(\text{XO}^\bullet) = aE_{\text{HOMO}}(\text{XO}^-, \text{AM1}) + b$ (Figure 3)	6	2–14, 16, 17	-0.52	0.63	0.991	15
	7	18–27, 29–33	-0.67	0.41	0.960	15
	8	40, 43–48	-0.55	1.28	0.970	7
	9	51–54, 57, 58	-0.51	0.92	0.990	6
$\Delta G_{\text{acid}}^0 = aE_{\text{HOMO}}(\text{AM1}) + b$ (Figure 4)	10	1–17	11.60	395.86	0.994	17
	11	18–27, 29–35	12.68	375.24	0.975	17
	12	40, 43–38, 50	14.60	392.92	0.982	8
	13	53–55, 57, 58	6.7	352.9	0.942	5
	14	2, 3, 12, 16, 17	4.74	39.73	0.994	5
$pK = aE_{\text{HOMO}}(\text{AM1}) + b$ (Figure 5)	15	19–21, 23–27, 29–31, 34–38, 41, 44–48	5.55	33.73	0.979	22

^aThe numbering of points corresponds to Table 1

pounds into three groups that are distinguished by their charge delocalization in the XO^- anion.

In a one-parameter relationship ΔG_{acid}^0 versus $EA(XO^-)$, the HOMO energy of the XO^- anion can be used on the basis of Koopmans' theorem, $EA = -E_{HOMO}$, for radical and anion,²⁹ instead of experimental values $EA(XO^-)$. For the calculations of vertical ionization energies of XO^- anions or the electron affinity of XO radicals (EA) in the present work, the semi-empirical methods MNDO, AM1 and PM3 were used.³⁰ These methods provide results (Table 1) that are comparable with respect to each other [equations (4) and (5) in Table 2]. Therefore, further correlation equations include only the calculated E_{HOMO} values which are obtained by means of the AM1 method (cf. Ref. 30). The dependences of the experimental values $EA(XO^-)$ on the calculated values E_{HOMO} (AM1) are presented in Figure 3. Any single class of compounds forms its own linear relationship with a unique slope [equations (6)–(9) in Table 2]. Since all slopes are less than unity, the E_{HOMO} values for XO^- anions are overestimated with respect to the experimental values of electron affinity $EA(XO^-)$ (cf. Ref. 30). The largest overestimation is characteristic of anions of mineral acids and the smallest overestimation of the calculated E_{HOMO} values belongs to aryloxy anions [equations (7) and (9) in Table 2]. A number of points deviate from lines I–IV (Figure 3). Thus, the point for the hydroxide ion (No. 1) falls above line I, that for the 3-nitrophenoxide ion (No. 28) falls above line II, the points for acetate ion (No. 41) and benzoate ion (No. 42) fall below line III and those for triflate ion (No. 59) and perchlorate ion (No. 60) fall above line IV. E_{HOMO} values for anions 1, 28, 59 and 60

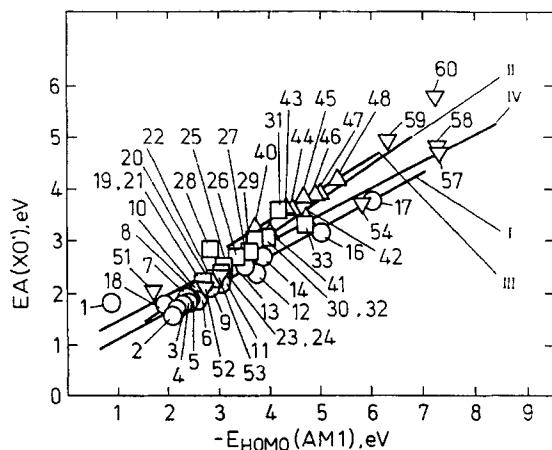


Figure 3. Dependences of electron affinity values of radicals XO (EA) on the HOMO energies of the corresponding XO^- anions (E_{HOMO}) (the numbering of points corresponds to the data of Table 1, equations (6)–(9) in Table 2; O, line I for alcohols; □, line II for phenols; △, line III for carboxylic acids; ▽, line IV for mineral acids)

underestimate the experimental values, while the calculated E_{HOMO} values for anions 41 and 42 overestimate the experimental values.

Since the relationships between experimental values $EA(XO^-)$ and calculated values E_{HOMO} (AM1) for XO^- anions in the framework of Koopmans' theorem describe only families of compounds, the dependences of ΔG_{acid}^0 on E_{HOMO} (AM1) [equations (10)–(13) in Table 2, Figure 4] separately describe the gas-phase acidity of alcohols, phenols, carboxylic and mineral acids. Point No. 28 deviates from line II (Figure 4), points 41, 42 and 49 deviate from line III and points 51, 52, 59 and 60 deviate from line IV, for the reasons mentioned above (Figures 2 and 3). It is possible that the OVGf (AM1) method for the estimation of E_{HOMO} values of anions, which is based on a modification of AM1 method,^{30d} can provide more precise convergence of experimental and calculated data. If this is verified, the XOH acidity could be described with a single equation:

$$\Delta G_{acid}^0 = cBDE(XO-H) + dE_{HOMO} + \text{constant} \quad (6)$$

where c and d are constants.

One might expect that the approach which is based on the quantitative description of gas-phase XOH acidity for some classes of compounds would be relevant also for the acidity of XOH acids in DMSO solution because it follows from the linear relationships between the XOH acidities in the gas phase and in DMSO solution.^{9,10,31} Both Table 2 [equations (14) and (15)] and Figure 5 present the dependences of the pK_a values of hydroxy acids in DMSO on E_{HOMO} of XO^- anions. The acidity of phenols and carboxylic acids corresponds

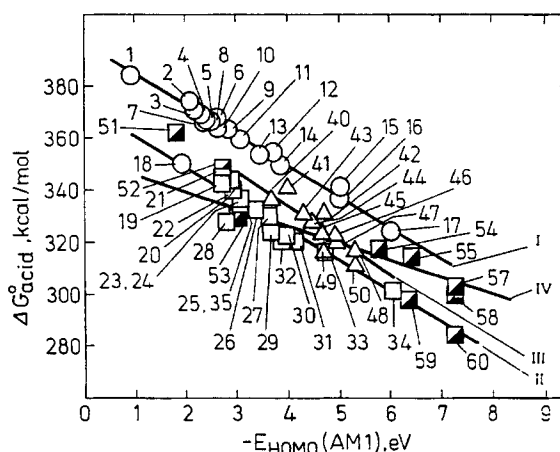


Figure 4. Gas-phase acidities of XOH acid series (ΔG_{acid}^0) versus HOMO energies of the corresponding XO^- anions (E_{HOMO}) calculated by AM1 method (the numbering of points corresponds to Table 1, equations (10)–(13) in Table 2; O, line I for alcohols; □, line II for phenols; △, line III for carboxylic acids; ▽, line IV for mineral acids)

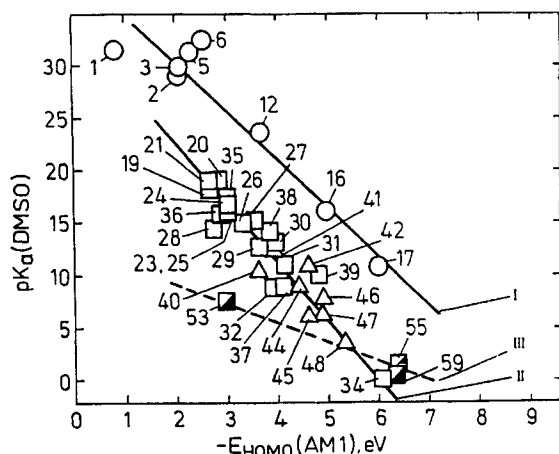


Figure 5. pK_a values of XOH acid series versus the HOMO energies of the corresponding XO^- anions (E_{HOMO}) calculated by AM1 method (the numbering of points corresponds to Table 1, equations (14), (15) in Table 2; O, line I for alcohols; □, △, line II for phenols and carboxylic acids; ■, line III for mineral acids)

to the same relationship [equation (15) in Table 2; Figure 5, line II]. Nevertheless, some deviations from these equations (points 1, 5 and 6 from line I and points 28, 32, 39, 40 and 42 from line II in Figure 5) are referred to the calculated values E_{HOMO} for these compounds.

In a previous study^{7a} on the estimation of the acidity of substituted phenols in DMSO, the oxidation potentials of phenoxide ions in DMSO were used. On this occasion, *para* substituents, being strong electron acceptors and donors, deviate from $E_{ox}(A^-)$ versus pK_a plots owing to additional stabilization of the phenoxyl radicals in solution.^{7a} There are no such deviations from the dependence of pK_a values on E_{HOMO} for phenols (Figure 5, line II) owing to the absence of this effect when using the calculated ionization energies for phenoxide ions.

For the mineral hydroxy acids, the acidity changes in DMSO are only slightly dependent on the E_{HOMO} values of their XO^- anions because of a lack of experimental data on pK_a (dashed line III in Figure 5).

Taking into account the wide structural variety of hydroxy acids, the application of the calculated E_{HOMO} values for the estimation of pK_a values for hydroxy acids of different classes in DMSO provides satisfactory results.

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