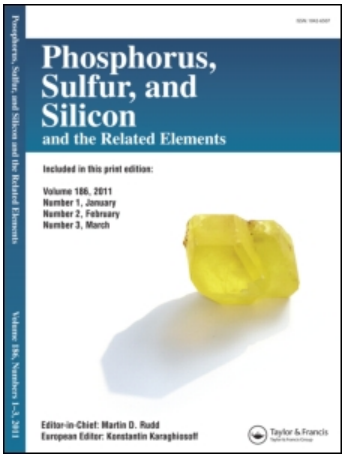

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ANALYSIS OF CH-ACIDITY OF ORGANOPHOSPHORUS COMPOUNDS

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Abstract The new "Three sigmas system" of $\sigma\rho$-correlation analysis by use of the Hammett equation was applied to organophosphorus CH-acids to yield good results.

INTRODUCTION

Many important reactions of organic chemistry are based on the CH-acidity of compounds, and some attempts were undertaken to make a $\sigma\rho$-correlation employing Hammett-Taft equations.[1] However the so called "Saturation effect" empeded constructing a system of such correlation. The effect of each substituent depends on the presence and the number of the other ones.[2] Solution of this problem seemed possible with the help of a new scale of σ - constants.

THREE SIGMAS SYSTEM

In the new scale, each substituent X is characterized by three constants depending on the first, secondary and tertiary substitution, as in the molecules XCH_3, XCH_2Y or XCHYZ (determination: σ^-_{CH3}, σ^-_{CH2} and σ^-_{CH}).[3] Application of the novel "three sigmas system" allowed to employ it successfully in more than 175 correlation series, including about 50 series of organophosphorus CH-acids, as well as to obtain 92% of excellent and good results (correlation coefficient 0.999 - 0.980).[4] In the "three sigmas system", calculations are performed by means of the usual Hammett equation $pK_a = pK_a^o + \rho\Sigma\sigma_{CHn}$

THE σ^-_{CHn} CONSTANTS OF ORGANOPHOSPHORUS GROUPS

Table 1 presents some σ^-_{CH2} values including the constants of organophosphorus groups. All σ^-_{CH2} constants may be divided into three groups.

TABLE 1 Selected σ^-_{CH2} data on π-acceptor groups

X	σ^-_{CH2}	X	σ^-_{CH2}	X	σ^-_{CH2}
NO_2	1.25	PhCO	0.98	$CONEt_2$	0.58
Ph_2S^+	1.23	MeCO	0.88	$Ph_2P(O)$	0.58
Ph_3P^+	1.22	CN	0.80	$(EtO)_2P(O)$	0.57
CF_3SO_2	1.10	Me_3N^+	0.79	$Bu_2P(O)$	0.46
Bu_3P^+	1.04	$Ph_2P(S)$	0.60	CF_3	0.40

To the first one belong substituents with the highest acidifying effect, among them are different R_3P^+-groups. To the groups of medium ability belong substituted thiophosphoryl groups. The majority of organophosphorus substituents belong to weak acidifying groups.

Of interest is the comparison of the acidifying ability of the onium groups - phosphonium, ammonium, sulfonium and arsonium (Table 2).[5]

TABLE 2 Selected σ^-_{CH2} data on onium groups R_nX^+

R_nX^+	N	P	As	S
Me_nX^+	0.79	0.94	0.90	1.02
Ph_nX^+	(1.06)	1.22	0.99	1.23
$C_5H_5N^+$	0.86			
$NC_4H_4N^+$	1.23			

Ammonium groups are substantially weaker than the phosphonium ones. This results from the absence of the resonance contribution in

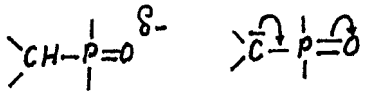
the effect. Phosphonium and sulfonium groups are approximately equal, and arsonium are somewhat inferior to them. The relations are controlled by the joint effect of three factors: inductive and resonance effects and bulk of groups. The pure inductive effect of the Me_3N^+ group is responsible for the σ^-_{CH2} value of 0,79. However a contribution from resonance carbanion stabilisation causes a substantial increase of the σ^-_{CH2} value (see the data for pyridinium and pyrazinium groups).

Table 3 presents σ^-_{CH2} and σ^-_{CH} constants of some substituted phosphoryl groups [5].

TABLE 3 Selected σ^-_{CH2} data on phosphoryl containing groups X

X	σ^-_{CH2}	σ^-_{CH}	X	σ^-_{CH2}	σ^-_{CH}
$Me_2P(O)$	0.47	0.35	$Et(EtO)P(O)$	0.52	-
$Et_2P(O)$	0.46	0.36	$Ph(EtO)P(O)$	0.56	-
$Bu_2P(O)$	0.46	0.34	$(EtO)_2P(O)$	0.57	0.44
t-$Bu_2P(O)$	0.44	-	$(PhO)_2P(O)$	0.60	0.47
$EtPhP(O)$	0.51	0.40	$(BuO)_2P(O)$	0.55	0.43
$Ph_2P(O)$	0.58	0.46	Ph_2P	0.43	0.44

Approximately equal acidifying effects of the grops $Ph_2P(O)$ and $(EtO)_2P(O)$ attract attention. These groups substantially differ in basicity, i.e. the ability to add proton. In the case of basicity, the major role is played by the value of the effective negative charge at the oxygen atom, but in the case of acidifying effect - the ability to delocalize the carbanionic charge:



Further note the acidifying action of thiophosphoryl groups is somewhat stronger than that of the corresponding phosphoryl groups. It

is interesting that the σ^-_{CH}-constants of diphenylphosphoryl and diphenylphosphine groups are approximately equal, but σ^-_{CH2} constants are not equal. Some particular but instructive relations will be published.[4]

With the help of the novel σ_p-correlation system we succeeded in analysing the literature data on the pK_a values of different organophosphorus CH-acids and kinetics of the Witting reaction. This system of correlations was successfully applied by us in the following studies: the phosphoryl group enolization (phosphoryl-phosphaenolic tautomerism) and CH-acidity of the corresponding phosphoryl compounds: $R_2P(O)\text{-}CHY\text{-}P^+Ph_3X^- \rightleftharpoons R_2P(OH)=CY\text{-}P^+Ph_3X^-$ [6], the Michael addition of vinylphosphinates to Shiff bases [7], acidic properties of phosphorylacetic acid amides, i.e. quite interesting extration reagents, $R_2P(O)CHR'\text{-}CONR''_2$ [8], and so on.

The application of the constants σ^-_{CH2} and σ^-_{CH} (and σ^-_{CH3}) for phosphorus-containing groups allows to evaluate quantitatively the acidifying effect and, consequently, a relative strength of organophosphorus CH-acids, irrespective of medium, and respectivly, stability and nucleophilic reactivity of the corresponding carbanions.

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