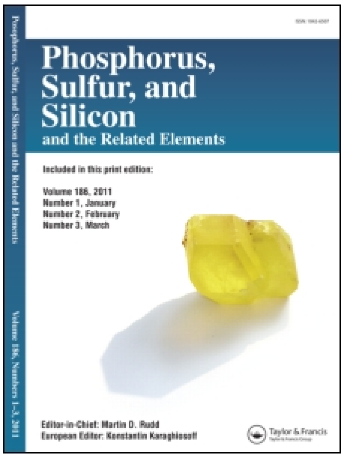

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A STUDY ON THE ADDITIVITY OF SUBSTITUENT EFFECTS IN THE TRIPHENYLPHOSPHONIUM SYSTEM

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Communication

A STUDY ON THE ADDITIVITY OF SUBSTITUENT EFFECTS IN THE TRIPHENYLPHOSPHONIUM SYSTEM

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Additivity of substituent effects in the methyl-triphenylphosphonium system with substituents on different phenyl groups is tested. Results show that additive linear free energy relationships can be applied to describe multiple substituent effects in this system.

Key words: Additivity substituent effects methyl-triphenylphosphonium system.

We report a study on the additivity of substituent effects in the triphenylphosphonium system with substituents at different phenyl groups. To test the applicability of additive Hammett equation, we considered the ^1H NMR chemical shift in $CDCl_3$ of methyl protons in methyl-substituted triphenylphosphonium salts, the ^{31}P NMR chemical shift in $CDCl_3$ of the same phosphonium salts and the rate constants for the nucleophilic substitution reaction with substituted phosphines on CH_3I in EtOH at 25°C.

Results are reported in Table I. In Table II are shown the results of the correlation by regression analysis.

It can be seen that the correlation of rate constants and δ^1H NMR chemical shift with $\Sigma\sigma$ is very good, with $r^2 = 0.998$ and 0.99 respectively. Correlation of $\delta^{31}P$ NMR chemical shift is poorer, with $r^2 = 0.944$. In this case we tried to apply additively the two parameters equation proposed by Swain et al., in our case $Y = f\Sigma F + r\Sigma R + h$. Using the five data for para-substituted phosphonium salts (^{31}P NMR chemical shift) we obtained $h = 22.8$, $f = 0.73$, $r = 0.75$ and $r^2 = 0.998$. So there is a significant improvement in the correlation. Substituent effects on the rate constants for nucleophilic displacement of iodide by phosphines on CH_3I are in relation with the interaction of substituents with the electrons pair on the phosphines and with the positive charge developed on the phosphorus atom in the transition state. In this case the correlation with $\Sigma\sigma$ is good ($r^2 = 0.998$) with $\rho = -1.23$, in agreement with a positive charge developed in the transition state. It is important to note that the monosubstituted compound fits the correlation together with the tris-substituted compounds. It is also relevant that from the study by Davies[3] on the reaction of para-substituted diethylphenylphosphines with ethyl iodide in acetone, an Hammett ρ value of $-1{,}11$ was calculated[4]; this value is similar to the one we have found in our tris-substituted system.

Correlation of δ^1H NMR chemical shift of our system with $\Sigma\sigma$ is good ($r^2 = 0.99$). Thus additive Hammett equation describes properly substituents effects transmitted up to the methyl hydrogens. Correlation of $\delta^{31}P$ NMR chemical shift

TABLE I

Rate constants, ^1H and ^{31}P NMR data

Substituents R[a]	$k \cdot 10^4$ [b]	$\lg k_R/k_H$	$\delta\, ^1H$ [c]	$\delta\, ^{31}P$ [d]	$\Sigma\sigma$ [e]
H	6.5	0	3.19	22.89	0
1-p-CH_3	13.3	0.311	3.12	22.54	-0.16
3-p-CH_3	29.5	0.66	3.035	21.79	-0.48
3-p-OCH_3	63.0	0.986	2.94	20.25	-0.84
3-p-Cl	0.96	-0.83	3.38	23.85	+0.66
3-m-CH_3	17.0	0.417	3.12	22.77	-0.21

a) Substituents on the phenyl groups in the para and meta position.

b) Second order rate constants in $dm^3\ mol^{-1}\ sec^{-1}$ for the reaction between substituted triphenylphosphines and CH_3I in EtOH at 25°C.

c) Chemical shift of methyl hydrogens in $CDCl_3$ at 25°C of methyl-substituted triphenylphosphonium iodide with Me_4Si as an internal standard.

d) Chemical shift of phosphorus in $CDCl_3$ (H_3PO_4/D_2O 85% as an external reference) at 25° C of methyl-substituted triphenylphosphonium iodide.

e) From ref. 2.

TABLE II

Parameters of linear regression analysis $Y = A_0 + A_1\Sigma\sigma$

System	A_0	A_1	R^2 [d]
1[a]	3.18	2.96	0.998
2[b]	22.74	2.29	0.944
3[c]	0.044	-1.237	-0.99

a) ^1H NMR chemical shift of methyl hydrogen of methyl-substituted triphenylphosphonium salts in $CDCl_3$.

b) ^{31}P NMR chemical shift of phosphourus of methyl-substituted triphenylphosphonium salts in $CDCl_3$

c) Second order rate constants for the reaction between substituted phosphines and CH_3I in EtOH at 25°C.

d) Correlation coefficient.

with $\Sigma\sigma$ is poorer ($r^2 = 0.944$); in this case the interaction of substituents with positive phosphorus is not completely described by Hammett σ. However application of the additive dual parameter equation shows good correlation and the ratio $f/r \simeq 1$ is an evidence that significant resonance contributions are involved.

In conclusion our data show that additive linear free energy relationships can be used to study multiple substituents effects on methyl-substituted triphenylphosphonium salts.

EXPERIMENTAL

Phosphines were commercial materials. Phosphonium salts were synthesized by reaction of appropriate phosphine with CH_3I in EtOH at 50°C. They were recrystallized from CH_3OH/Et_2O. ^1H NMR spectral data ($CDCl_3$). Methyl-triphenylphosphonium iodide; δ 3.19 (d, J = 13.19 Hz, CH_3), 7.6 (m, C_6H_5). Methyl-*p*-tolyl-diphenylphosphonium iodide, δ 2.46 (s, CH_3), 3.12 (d, J = 13.18 Hz, CH_3), 7.6 (m, $1C_6H_5$, $2C_6H_4$). Methyl-tris-*p*-tolyphosphonium iodide, δ 2.5 (s, $3CH_3$), 3.035 (d, J = 13.12 Hz, CH_3), 7.6 (m, $3C_6H_4$). Methyl-tris-*p*-methoxyphenylphosphonium iodide, δ 3.9 (s, $3CH_3$), 2.94 (d, J = 13.15 Hz, CH_3), 7.4 (m, $3CH_5H_4$). Methyl-tris-*p*-chloro phenylphosphonium iodide, δ 3.38 (d, J = 13.7 Hz, CH_3), 7.8 (m, $3C_6H_4$). Methyl-tris-*m*-methylphenylphosphonium iodide, δ 2.47 (S, $3CH_3$), 3.12 (d, J = 13.1 Hz, CH_3), 7.55 (m, $3C_6H_4$). ^1H NMR spectra were recorded on a Bruker WP80 spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ with H_3PO_4/D_2O (85%) as external reference on a Bruker AC200 spectrometer.

Kinetics. Second order rate constants in $dm^3\ m^{-1}\ s^{-1}$ were calculated for the reaction between the aromatic phosphines and CH_3I in EtOH at 25°C by the kinetic expression $1/a\text{-}x - 1/a = kt$. Concentration of reactants were $\simeq 0.01$ M. Reactions were followed by potentiometric titration with $AgNO_3$ of iodide produced.

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