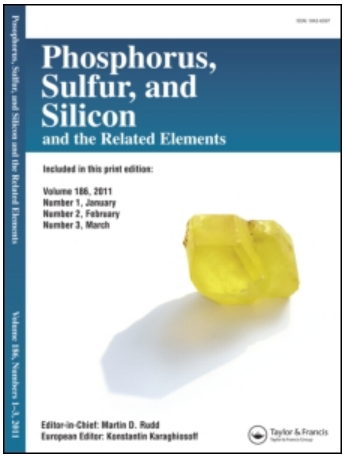

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Galkin, V. I. , Cherkasov, A. R. and Cherkasov, R. A.(1999) 'Modelling of Substituents Electronic and Steric Effects for Effective Analysis of Organoelement and Organophosphorus Reactivity', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 329 — 332
To link to this Article: DOI: 10.1080/10426509908546248
URL: http://dx.doi.org/10.1080/10426509908546248

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 329-332
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Modelling of Substituents Electronic and Steric Effects for Effective Analysis of Organoelement and Organophosphorus Reactivity

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For the effective analysis of organic and organoelement reactivity and the reaction mechanisms we have elaborated a simple enough models of steric and inductive substituents effects, which allow to calculate theorically the steric and inductive constants of any substituent at any reactive center. Both of these models possess of clear and comprehensible physical meaning, their correctness was confirmed by a good agreement of theorically calculated constants with well-known experimental steric and inductive scales. The wide possibilities of the suggested models for investigation of reaction mechanisms, organic and organoelement (organophosphorus, in particular) reactivity are discussed on the basis of different important organophosphorus reactions Pudovik, Abramov, Willyamson, Kabachnic-Fields reactions, acidic-basis equilibria, addition and complexation processes, etc.)

INTRODUCTION

The relationship between the structure of organic and organoelement compounds and their reactivity is one of the fundamental problems of contemporary chemistry. It is evident now that the most correct information concerning organic reactivity and reaction mechanisms may be obtained only on the basis of quantitative approaches describing intramolecular interactions, that is (in terms of correlation analysis) interactions between any substituent and the reactive center. At present, the overall interaction of a substituent with a reactive center is conventionally subdivided into inductive, resonance, and steric components; the impossibility of isolating each of these correctly is nowadays one of the main obstacles to further development of quantitative organic chemistry and correlation analysis. In the present work, we report about our results in elaboration of relatively simple models of the steric and the inductive effects which, being based on an available body of mathematics, allow to calculate theoretically the steric and inductive constants of any substituent at any reactive center. The application of the suggested approaches for analysis of organic

and organoelement reactivity and reaction mechanisms (generally on example of different organophosphorus reactions) will also be considered.

Model of Frontal Steric Effect

Elaborated model of frontal steric effect and its mathematical apparatus are presented in detail in works [1-3] , so here we shall limited only by their short description. The suggested steric model is based on the concept about simple mechanical screening of a reactive center by a substituent, i.e about the frontal nature of steric effect (fig.1).

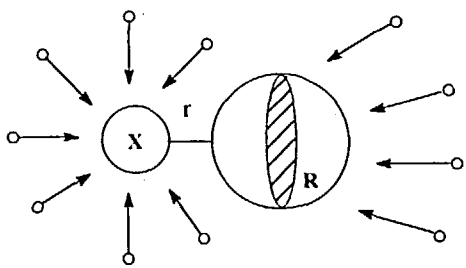

Fig.1. Attack on the substituted reaction center

In the framework of the kinetic theory of active collisions it is easy to show that the substituent steric effect is propotional to the square which it occupies on the sphere, separating its from reaction center, the rate constant being described by expression (1):

$$k = (1 - \sum_{i=1}^{n} R_i^2 / 4r_i^2) Z \exp(-E/RT) \qquad (1),$$

where Z is frequency of pairwise collisions, E is activation energy, R_i is a radius of every concrete atom in polyatomic substituent, and r_i is the distance between the substituent and the reactive center.

We have suggested also purely estimating steric scale R_S , which had been introduced as expression (2).

$$R_S = 30 \lg \left(1 - \sum_{i=1}^{n} R_i^2 / 4r_i^2\right) \qquad (2).$$

This scale well correlates with empirical scales, adequitly describing the steric effect of various substituets [1-3].

Our experience accumulated in studying the steric effect indicates very high efficiency of the model not only to calculate adequately and with high accuracy the steric effect of any substituent at any reactive center, but also to solve many other problems that are intractable or hard-to-solve problems in terms of the existing empirical scales. For instance these are such important problems as separation of steric and electronic effects, the isostericity principle, the sensitivity of organoelement reactive center to the substituent steric effect, dependence of steric effect on substituent conformation, and many others up to the thin questions of dynamic stereochemisrty and transition state structure [1-5].

A New Model of Inductive Effect

For the effective analysis of intramolecular electronic interactions we have elaborated also a new formal model of inductive effect enabling highly accurate theoretical calculations of any inductive constants for a diversity of substituents, using the following additivity equation (3) [6]:

$$\sigma^* = \sum_{i=1}^{n} (\sigma_A)i / r_i^2 \qquad (3),$$

Here σ^* - is the inductive constant of a substituent in the Taft scale; n - is the number of atoms in the substituent; r_i - is the distance from i-th atom of substituent to the reaction center; σ_A - is the inductive power of i-th atom, which depends on the chemical nature of the element and its valence state.

The proposed additive approach describes with a high degree of accuracy the inductive constants of quite a variety of organic, organoelement and charged substituents for nearly the whole available body of s constants (eq. 4).

$$\sigma^*_{theor.} = (-0.031 +/- 0.012) + (0.993 +/- 0.006)\, \sigma^*_{exp.} \qquad (4)$$

$$N = 426 , R = 0.9910 , S = 0.190 .$$

The inductive model suggested allows to solve many important and interesting questions - such as that about an absence or presence of the linearity in the substituents inductive effect in organic and organoelement chemistries, inductive influence of alkyl groups, non-quantum-chemical calculation of partial charges on molecule's atoms, estimation of group electronegativities (that is especially interesting for organometallic chemistry) and, at last, the problem of effective analysis of organoelement (organophosphorus, in particular) reactivities and reaction mechanisms [6-8].

Thus it should be noted that modelling of substituents effects is a perspective approach, and suggested models of steric and inductive effects being simple and correct may be very helpful for quantitative analysis of organic and organoelement reactivity and reaction mechanisms for various reaction independently on the nature reaction center and substituents.

Acknowledgments

The work is realized under financial support of Russian Fond of Fundamental Investigations (grant N 96-03-32864a) and Scientific Program «Russian Universities».

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