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Taft equation in the light of NBO computations. Introduction of a novel polar computational substituent constant scale σ_q^* for alkyl groups

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ABSTRACT

The validity of the Taft equation: $\log(k_R/k_{CH3}) = \rho^*\sigma^* + \delta E_S$ was studied with the aid of NBO computational results concerning cyclohexyl esters $RCOOC_6H_{11}$ [R = Methyl, Ethyl, *n*-Propyl, Isopropyl, *n*-Butyl, Isobutyl, *sec*-Butyl, *tert*-Butyl, Neopentyl, $CH(CH_2CH_3)_2$, $CH(CH_3)C(CH_3)_3$, $C(CH_3)_2CH_2CH_3$, $C(CH_3)_2C(CH_3)_3$, $CH(CH_3)(Np)$, CH(iPr)(tBu), C(Me)(Et)(iPr), $C(Et)_2(tBu)$ or C(Et)(iPr)(tBu)]. It was proved that the σ^*(alkyl) value is a composite substitutent constant including the polar and steric contributions. A novel computational σ_q^* substituent constant scale is presented based on the NBO atomic charges of the α-carbon and the computational total steric exchange energies E(ster) of the cyclohexyl esters specified above. The method used offers a useful way to calculate σ^*(alkyl) values for alkyl groups for which experimental Taft's polar σ^* parameters are not available.

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1. Introduction

The concept of the polar effect, also known as electronic effect, is of great importance in chemistry. The physicochemical interpretation of the polar effect relies on different concepts, such as inductive effect, conjugation, orbital symmetry and through-space electrostatic interactions. It is often thought that the polar effect is exerted by a substituent by means of modifying electron density at a nearby probe center. The polar effect contrasts with the steric effect, i.e. the steric hindrance near the reaction center or the steric repulsions between different atoms or groups of a molecule. Polar and/or steric effects may affect the molecule's reactivity, conformation or physicochemical properties. Each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, an associated repulsion occurs due to the overlapping electron clouds (Pauli or Born repulsion). Characterization of a prevailing effect may be difficult, because both steric and polar effects, at least partly, rely on repulsive/attractive electrostatic interactions. The task is still complicated by the fact that the probability of both these effects increases with the increasing size of a substituent. However, by using experimental methods several attempts have been made to create quantitative substituent parameter scales which describe the polar or steric effects of the certain substituent on the properties of a molecule.

Taft used the hydrolysis of methyl esters (RCOOMe) for quantification of the polar and steric effects. The Taft equation (Eq. (1)) is a dual substituent parameter equation which consists of the polar σ^* and steric E_S substituent constants [1]. k_R or k_{CH3} refer to the reaction rate constant

$$\log(k_R/k_{CH3}) = \rho^*\sigma^* + \delta E_S \tag{1}$$

when R is an alkyl group or the reference methyl group, respectively. The evaluation of the contributions of the polar (ρ^*) and steric (δ) effects on the reaction studied is possible with (Eq. (1)). Determination of the σ^* and E_S constants is based on the following assumptions. The acid catalyzed and alkaline ester hydrolysis give transition states with different charge distributions for the rate determining steps. However, their structures if R is same differ only by two hydrogen atoms (Scheme 1a and 1b). Taft assumed therefore that the steric effects on the rates of both reactions are similar and that the polar effects are only observable in the reaction rate of the alkaline hydrolysis where a new charge is generated in the transition state. Due to the latter assumption, the acid catalyzed hydrolysis reaction, where the rate constants are not sensitive to polar effects (Eq. (2)), was used to determine the steric E_S parameter. The polar substituent constant σ^* was obtained as the difference shown in Eq. (3) (the Taft–Ingold equation) where the subscripts A and B refer to the acid catalyzed and alkaline ester hydrolysis, respectively [1]. The factor 2.48 places σ^* on about the same scale as the Hammett σ values.

$$E_s(R) = \log(k_R/k_{CH3})_A \tag{2}$$

$$\sigma^* = 1/2.48[\log(k_R/k_{CH3})_B - \log(k_R/k_{CH3})_A] \tag{3}$$

The Taft equation is widely used. Besides kinetic data different other types of experimental characteristics, such as spectroscopic properties, or computational parameters, often give good correlations with

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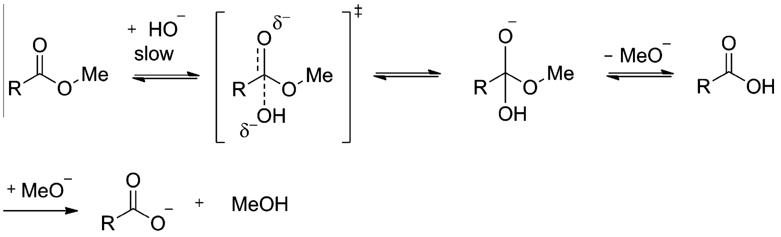
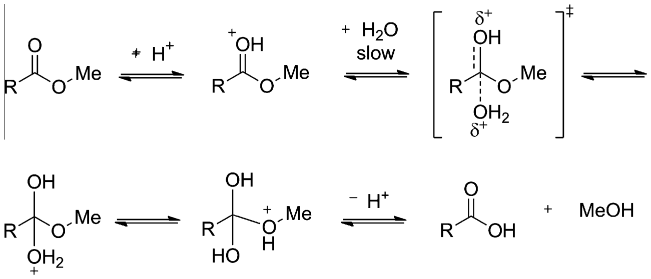


Scheme 1a. Mechanism of the alkaline ester hydrolysis.



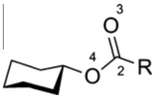
Scheme 1b. Mechanism of the acid catalyzed ester hydrolysis.

σ^* and E_S constants of a substituent. The Taft-Dubois steric parameter E'_S, closely related to the Taft's original E_S values, has later become one of the standard measures of steric effect [2].

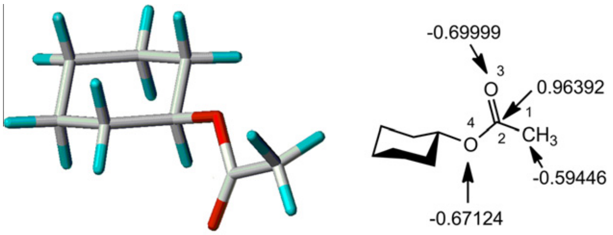
The Taft equation is a postulate. There is no unambiguous proof to the effect that the σ^* and E_S constants represent pure polar (electronic) and steric effect, respectively. Because the E_S and related values may include a component of electronic effects, computational steric parameter scales which are not dependent on the experimental kinetic data have been established. Charton has presented the v values based on the van der Waals radii of the substituent [3]. Meyers has defined V^a values that are derived from the computed volume of the portion of the substituent that is within 0.3 nm of the reaction center [4]. In principle, Taft's E_S(R) value reflects the size dependent steric hindrance of the R group when a reagent molecule approaches the C=O reaction center. Solid angles have also been used to quantify the steric hindrance giving the Ω_S substituent parameter scale [5]. The ligand repulsive energies offer an alternative computational route, too, and the E_R substituent constant scale is derived on this basis [6]. To our knowledge, there is, however, no computational substitute for the Taft's σ^* substituent scale. The fact that relatively few σ^* values in comparison with the E_S or related values are available for alkyl groups emphasizes the need of a computational polar substituent parameter scale. In a computational work dealing with the conformational equilibrium of cyclohexyl esters of aliphatic carboxylic acid we were able to demonstrate that the q_C(C=O) atomic charge depends systematically on the α-substitution R for a series where R = Me, Et, iPr or tBu [7]. This prompted us to devise a novel polar substituent constant scale for alkyl groups by using natural bond orbital analysis. Besides, our goal was to advance the understanding of the nature of Taft's σ^* constant and of the interdependence of the σ^* and E'_S constant with the aid of the NBO computations.

2. Experimental

We have employed the *ab initio* second-order Møller–Plesset perturbation (MP2) [8] and density-functional theory (DFT) [9] approaches for the molecules of the set given in Scheme 2a. The DFT scheme utilized Becke's three-parameter functional (B3LYP) [10]. The computations were performed using the Gaussian 03 program package [11]. Different levels of theory were previously tested. The results at the MP2/6-311 + G*//MP2/6-311G* theoretical level including electron correlations [8] proved to be the most reliable and were therefore used to calculate the energies of the fully relaxed structures. The NBO 5.G population analysis [12] compiled in the Gaussian 03 package, was performed on the MP2 density [8]. The NBO steric analysis (STERIC) was carried out at DFT – B3LYP/6-31 + G* level of theory [13]. The 3D structure (Scheme 2b) was displayed using SYBYL7.3 molecular modelling software [14]. The substituent (R) sensitivity of the natural atomic charge values (q) and/or the total steric exchange energy values [E(ster)] of the cyclohexyl esters ($RCOOC_6H_{11}$) were analyzed using various types of correlations and cross-correlations. The steric E'_S and the σ^* polar substituent parameters used in the correlations are from Refs. [2] and [1], respectively. Table 1 gives the natural atomic charge values (q) for the —O—C(=O)—C function of the cyclohexyl esters (cf. Scheme 2a). The different steric substituent constant scales are compared in Table 2 by correlation with the computed q values. A compilation is given in Table 3 for the correlation data of some experimental or computational parameters (P) against the E'_S and σ^* constants or the computed q_C(C=O) values (A) by using equation $P = \rho A + k$. The slope values and correlation coefficients are included. Table 4 lists the values for different alkyl substitutions in the novel σ^*_q substituent constant scale.



Scheme 2a. List of cyclohexyl esters of aliphatic carboxylic acids studied. R = Methyl (Me), Ethyl (Et), *n*-Propyl (*n*Pr), Isopropyl (iPr), *n*-Butyl (*n*Bu), Isobutyl (iBu), *sec*-Butyl (sBu), *tert*-Butyl (tBu), Neopentyl (Np), $CH(CH_2CH_3)_2$, $CH(CH_3)C(CH_3)_3$, $C(CH_3)_2CH_2CH_3$, $C(CH_3)_2C(CH_3)_3$, $CH(CH_3)(Np)$, CH(iPr)(tBu), C(Me)(Et)(iPr), $C(Et)_2$(tBu) or C(Et)(iPr)(tBu).



Scheme 2b. Minimum energy conformation and natural atomic charges of cyclohexyl acetate.

3. Natural atomic charges and polarization of the OC(O)C(α) unit

For all $RCOOC_6H_{11}$ molecules studied, the carbonyl carbon (C2) exhibits a positive atomic charge (q) value and the ether (O4) and carbonyl oxygens (O3) as well as the α-carbon (C1) negative ones

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