CHEMISTRY

An Attempt at Calculating the Taft's Constants σ^*

In our study of the influence of structure on the reactivity and properties of non-aromatic compounds in homologous series we have investigated the possibility of calculating Taft's[1] polar substituent constants σ^*. It is well known that there exists a connexion between the electron density on the carbon atom (C_f) to which the functional group is linked and the value of σ^*.

We obtained a very close correlation between these two quantities when the electron densities were calculated by means of a very simple method recently proposed by Del Re[2]. The dependence is linear. The data for saturated, non-substituted derivatives lie on one straight line, while the data for substituted alkyls are situated on another (Fig. 1), consequently

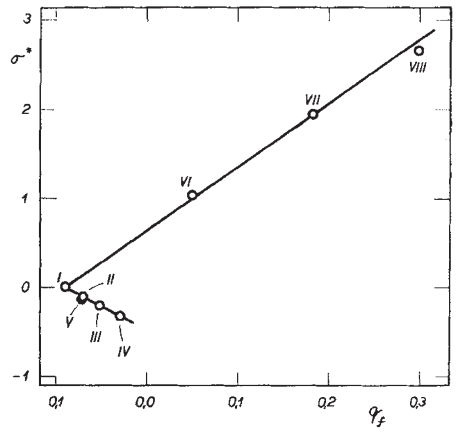

Fig. 1. The dependence of Taft's σ^* constants on the electron density on the carbon atom C_f: I, methyl; II, ethyl; III, isopropyl; IV, *tert* butyl; V, *n*-propyl; VI, chloromethyl; VII, dichloromethyl; VIII, trichloromethyl

the relation between the electron densities according to Del Re and Taft's σ^* constants is defined by:

$$\sigma^* = a + bq_f \qquad (1)$$

where a and b are numerical constants, which are negative for the first group of substituents (alkyls) and positive for the second group (Table 1) and q_f is the electron density on C_f. This relation is formally the same as the one found by us[4] for the connexion between the basicity or the position of the absorption maximum of N-alkylthioureas and the constants σ^*.

By means of equation (1) we can, on one hand, predict the values of σ^* for substituents for which this value has not been determined from experimental data and, on the other hand, verify or propose the values of the empirical parameters occurring in the above mentioned method[2]. Further details will be published later.

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Estimation of Chain Fracture and Cross-Linking of Rubber by High-energy Radiation

Recently the solubility behaviour of irradiated polymers has been analysed theoretically by Charlesby and Pinner[1]. The soluble fraction (s) of a cross-linked network of macromolecular material, initially of randomly distributed molecular weights, can be written:

$$s + s^{1/2} = \frac{p}{q} + \frac{1}{\delta_n} \qquad (1)$$

where δ_n, the cross-linking coefficient, is the average number of cross-linked units per number average molecule, and p and q are the fracture and cross-linking densities respectively. Assuming that p and q are proportional to the radiation dose r, then the sol fraction is related to the densities of fracture per unit dose (p_o) and cross-links per unit dose (q_o), by the equation:

$$s + s^{1/2} = \frac{p_o}{q_o} + \frac{1}{q_o\, u_1\, r} \qquad (2)$$

where u_1 is the number average degree of polymerization. Charlesby and Pinner applied their treatment to experimental results on polyethylene, polyvinyl acetate and other polymers.

Expression 1 may be applied without making assumptions regarding the dependence of p and q upon the radiation dose.

Lightly masticated pale crepe rubber, which had been freshly extracted with acetone, was evacuated and sealed in glass tubes. After irradiation, with gamma radiation from a cobalt-60 source or a linear electron accelerator, the soluble fraction was measured by extraction of the samples with benzene. In each case, the mean intensity of the radiation was estimated by ferrous sulphate dosimetry ($G_{Fe(3+)} = 15{\cdot}6$).

Solubility data for the gamma irradiation of rubber at two dose-rates at 25°C., quantitatively analysed in the manner adopted by Charlesby and Pinner, are shown in Fig. 1. Experimentally, the $s + s^{1/2}$ values diverge from the straight line drawn through data relating to high doses. Presumably the initial distribution of molecular weights is not perfectly random and some dislinking is necessary to attain this.

Fig. 1 shows that the rate of cross-linking is directly proportional to the intensity of radiation, similar to the behaviour of polyethylene[2] and other polymers. The G-value of the cross-linking reaction, calculated

Table 1. Published and calculated values of σ^*

Alkyl	Methyl	Ethyl	*iso* Propyl	*tert* Butyl	*n*-Propyl	Chloro-methyl	Dichloro-methyl	Trichloro-methyl
Refs. 1 and 3	0·000	−0·100	−0·200	−0·320	−0·115	1·050	1·940	(2·65)
Calculated by equation 1†	−0·008	−0·109	−0·204	−0·326	−0·101	0·996	1·931	2·752

† Values of numerical constants a and b (equation 1): $a = -0{\cdot}485$ and $b = -5{\cdot}30$ for saturated, nonsubstituted substituents, and $a = 0{\cdot}642$ and $b = 7{\cdot}08$ for the second group of substituents.