Correlation between Taft σ^* Constants and Information Entropy in Aromatic Substitution Reactions

1965

SovietRxiv

Abstract

Full Text

Chemistry

Yu. A. Zhdanov

Correlation between Taft σ^* Constants and Information Entropy in Aromatic Substitution Reactions

(Presented by Academician A. N. Nesmeyanov, February 11, 1965)

Earlier ([1]) we showed that information entropy can serve as a measure of specificity in aromatic substitution reactions. In accordance with Shannon' s formula ([2]), the information entropy (or distribution entropy) for the products of subsequent substitution of monosubstituted benzenes is determined by the formula:

$$H_s = -p_o \log p_o - p_m \log p_m - p_n \log p_n, \tag{1}$$

where p_o, p_m, p_n are the molar fractions of the individual isomers (i.e., $p_o + p_m + p_n = 1$)*. Obviously, the quantity H_s expresses a measure of uncertainty in the course of the substitution reaction; its value is maximal when the yields of the isomers are equal and is equal to zero when only one product is formed.

It is of interest to establish a relationship between information entropy and quantitative characteristics of substituents in the benzene nucleus. To this end we compared the value of H_s with Taft's polar (inductive) constant σ^* ([3]). Data for the nitration reaction in acetic anhydride at 25° are presented in Table 1. It follows from the data of this table that a decrease in the value of σ^* entails an increase in the uncertainty of the course of the reaction. The value of H_s begins to fall when we pass to alkyl substituents that donate electrons to the benzene ring by the inductive mechanism $+I$.

Table 1

Ph –R	σ^*	H_s exp.	H_s calc.	ΔH_s	Ph –R	σ^*	H_s exp.	H_s calc.	ΔH_s
$+NMe_3$	5.3	0.0000	−0.0016	−0.0016	HO	1.55	0.2922	0.3489	+0.0567
NO_2	3.9	0.1129	0.1292	+0.0163	OCH_3	1.45	0.3353	0.3582	+0.0229
CN	3.6	0.1707	0.1573	−0.0134	$NCCH_2$	1.3	0.3615	0.3722	+0.0107
F	3.1	0.1731	0.2040	+0.0309	FCH_2	1.1	0.4342	0.3909	−0.0433
Cl	2.9	0.2156	0.2226	+0.0070	$ClCH_2$	1.05	0.4234	0.3956	−0.0278
COOH	2.9	0.2369	0.2226	−0.0143	CH_3	0.00	0.3548		
Br	2.8	0.2874	0.2320	−0.0554	C_2H_5	−0.10	0.3856	0.3809	−0.0047

Ph–R	σ^*	H_s exp.	H_s calc.	ΔH_s	Ph–R	σ^*	H_s exp.	H_s calc.	ΔH_s
I	2.36	0.2939	0.2732	−0.0207	iso-C_3H_7	−0.19	0.3706	0.3650	−0.0056
$CO_2C_2H_5$	1.87	0.3167	0.3196	+0.0029	tert.-C_4H_9	−0.30	0.3353	0.3543	+0.0190
CH_3CO	1.65	0.3047	0.3395	+0.0348					

By the method of least squares we calculated the correlation between H_s and σ^* separately for two groups of substituents: those having positive and negative values of σ^*. For the first group of substituents it turned out that the quantity H_s is related to σ^* by a linear dependence

$$H_s = 0.4937 - 0.09345\,\sigma^*. \tag{2}$$

* The positions o and o', as well as m and m', are taken as indistinguishable.

The correlation coefficient is $r = 0.96$. The calculated values of H_s correlate quite satisfactorily with the experimental data. For alkyls with negative values of σ^*, the equation $H_s = 0.3985 + 0.1765\sigma^*$ was obtained. In this series the correlation is weaker: $r = 0.7$. In all cases we excluded from the calculation the data for the CH_3 group ($\sigma^* = 0.0$), which

Table 2

Ph–R	σ^*	H_s, expt.	H_s, calc.	ΔH_s	Ph–R	σ^*	H_s, expt.	H_s, calc.	ΔH_s
NO_2	3.9	0.2346	0.2382	+0.0036	NHAc	1.78	0.2653	–	–
CN	3.6	0.2750	0.2654	−0.0096	OH	1.55	0.3006	–	–
Cl	2.9	0.3122	0.3290	+0.0168	OCH_3	1.45	0.2874	–	–
Br	2.8	0.3485	0.3381	−0.0104	CH_3	0.0	0.2955	–	–

sharply deviates from both series (in the first series $\Delta H_s = 0.1389$; in the second $\Delta H_s = 0.0437$). This is also evident from Fig. 1, in which nitration is shown by the solid line and chlorination by the dashed line.

A somewhat different picture is observed for the chlorination reaction in acetic acid, as follows from the data in Table 2.

In this table, the presence of two groups of substituents is noteworthy. The first group includes NO_2, CN, Cl, and Br. As for the nitration reaction, here we observe a linear increase in the value of H_s as the substituent σ^* decreases. This dependence is well described by the equation

Fig. 1: plot of H_s versus σ^*; dashed line—chlorination, solid line—nitration.

Figure 1: Fig. 1: plot of H_s versus σ^*; dashed line—chlorination, solid line—nitration.

reaction scheme (5)

Figure 2: reaction scheme (5)

$$H_s = 0.5923 - 0.0908\sigma^*. \tag{3}$$

In the present case the correlation coefficient is very high, $r = 0.992$.

The behavior of the second group of substituents—NHAc, OH, OCH_3, CH_3—is distinctive. Here H_s is practically independent of σ^*; the process is characterized by approximately constant uncertainty of occurrence for different substituents, while the experimental values of H_s lie considerably below those calculated by formula (3).

Fig. 1

The regular change in H_s as a function of the substituent σ^* value in nitration reactions confirms the assumption of a single mechanism for this reaction for various substituted benzenes ([4]). This mechanism is associated with the initial formation of the nitronium cation, which attacks the aromatic nucleus, first forming a π-complex (I), and then a σ-complex (II), which subsequently decomposes to the final product:

$$\mathrm{R{-}C_6H_5} \xrightarrow{+\mathrm{NO_2}} \text{(I)} \rightarrow \text{(II)} \xrightarrow{-\mathrm{H^+}} \mathrm{R{-}C_6H_4{-}NO_2} \tag{4}$$

For the chlorination of substituted benzenes with Cl_2, a single mechanism ([4]) is usually also considered, which assumes attack of the aromatic nucleus by a chlorine molecule with the participation of a polar solvent (A).

(5)

However, on the basis of the data presented, it may be assumed that chlorination proceeds in the benzene ring by two routes. Of these, the first is close to the mechanism of nitration: attention is drawn to the parallel course of the nitration and chlorination plots, which makes it possible, from equations (2) and (3), to write the fairly exact relation

$$H_s(\text{chlor.}) = H_s(\text{nitr.}) + 0.1.$$

reaction scheme (6)

Figure 3: reaction scheme (6)

It may be assumed that in this case, under the influence of the strong polar effect of the substituent already present in the benzene ring (high values of σ^*), a π-complex (I) is initially formed, which, under the influence of the electron-donating substituent R, undergoes heterolytic decomposition with formation of the π-complex (I′); the latter, behaving analogously to the π-complex with the nitronium cation, rearranges into a σ-complex with the lesser degree of orientation (larger value of H_s), the lower the magnitude of σ^*.

(6)

For chlorination reactions of the second type, mechanism (5) should be considered more probable, in which the decisive role belongs to the electromeric effect $+E$. This explains the absence of a pronounced dependence of H_s on variation of σ^* and, at the same time, the high specificity of the process. The existence of two chlorination mechanisms is also indicated by the data on relative substitution rates (5). For reactions of the first type ($-I$-effect stronger than the $+F$-effect), the values of K_R/K_B lie in the range 10^{-2}-10^{-1}; for reactions of the second type they reach 10^6-10^7. In this case the $+E$-effect of the substituents considerably exceeds their inductive action.

Rostov-on-Don
State University

Received
8 II 1965

CITED LITERATURE

1. Yu. A. Zhdanov, Zh. Fiz. Khim., **39**, No. 3 (1965).

2. C. Shannon, *Works on Information Theory and Cybernetics*, Moscow, 1963.

3. V. A. Palm, *Russ. Chem. Rev.*, **30**, 1069 (1961).

4. H. Becker, *Einführung in die Elektronentheorie organischchemischen Reaktionen*, Berlin, 1961.

5. L. M. Stock, H. C. Brown, *Advances in Physical Organic Chemistry*, **1**, 1963.

Note: Figure translations are in progress. See original paper for figures.