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Abstract

Full Text

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APPLICATION OF THE TAFT EQUATION TO THE HYDRIDE-TRANSFER REACTION IN AN ACIDIC MEDIUM

(Presented by Academician V. N. Kondratʹ ev on 31 V 1961)

In recent years there has been a great increase in interest in the Hammett equation

$$\lg k = \lg k_0 + \rho\sigma \tag{1}$$

as a basis for establishing the relationship between the structure of compounds and their reactivity. This was greatly facilitated by the studies of Taft (^{1}) and Jaffé (^{2}), which made it possible to extend substantially the range of applicability of relationships of type (1) to polynuclear aromatic compounds with several substituents in the ring, on the one hand, and to aliphatic compounds, on the other. It became possible to take into account the effect of polar conjugation of the substituent with the reaction center (σ^+) (^{3}). The latter is very important in reactions involving aromatic carbonium ions. The new possibilities stimulated the appearance of a large number of studies on the application of the Hammett-Taft relationship to reactions of various types, often without taking into account that these relationships are meaningful only when applied to simple reactions. In the case of complex reactions whose mechanism is unknown, the fact that a linear dependence between the logarithm of the observed rate constant and σ (or σ^+) is or is not fulfilled gives no grounds for far-reaching conclusions about the nature of the process.

Fig. 1. Dependence of $\lg k_{\mathrm{eff}}$ on the concentration of H_2SO_4 at 90° for carbinols: 1—TPK, 2—DPTK, 3—DTPK, 4—DAPK.

A necessary condition for the proper application of the Hammett-Taft rule to a complex reaction is knowledge of the mechanism of this reaction; the rule should be applied to the rate constants and equilibrium constants of the individual stages.

The validity of this statement will be shown below by the example of applying the Taft relationships to the reaction of reduction of four triarylcarbinols (TAC) by isopropyl alcohol via hydride transfer in an acidic medium. It should be noted that in the literature there is only one study (^{8}) applying relationship (1) to hydride-transfer reactions.

As a result of a detailed study of the kinetics of reduction by isopropyl alcohol in a sulfuric acid medium of triphenylcarbinol (TPK) and its derivatives: diphenyl-*m*-tolylcarbinol (DPTA), di-*p*-tolylphenylcarbinol (DTPK), di-*p*-anisylphenylcarbinol (DAPK)—there were obtained

values of the effective rate constants of the reaction in the temperature range from 35 to 90°C and at H_2SO_4 concentrations from 4 to 60% ($^{4-6}$). As was shown previously (^{7}), these reactions proceed by transfer of a hydride ion from the alcohol to the carbinol according to the overall equation:

$$\mathrm{Ph_3COH + iso\text{-}C_3H_7OH \xrightarrow{H^+} Ph_3CH + (CH_3)_2CO + H_2O.}$$

The magnitude of the effective rate constant k_{eff} of the hydride-transfer reaction depends on the acid concentration. This dependence has an extremal form (^{4,5}).

Table 1

Values of $k^*_{\mathrm{eff}} \cdot 10^3$ (l/mol • sec) at 90°

Substituents	σ^+	30% H_2SO_4	38% H_2SO_4	56% H_2SO_4
H(TPC)	0	1.53	11.60	36.60
m-CH_3(DTPC)	0.066	0.72	6.72	18.15
n-CH_3(DTPC)	−0.311	5.24	19.05	2.02
n-OCH_3(DAPC)	−0.778	1.31	0.91	0.065

* Values of the constants calculated from equation (2).

Figure 1 presents the dependence of $\lg k_{\mathrm{eff}}$ on the acid concentration for four carbinols. Since experimental values of k_{eff} were not obtained for all carbinols over the entire range of H_2SO_4 concentrations, Fig. 1 gives values of the constants calculated by formula (2).

Even at a cursory glance at Fig. 1 it is evident that the order of variation of the effective rate constants of the four carbinols depends on the H_2SO_4 concentration at which k_{eff} is compared.

Fig. 2. Dependence of $\lg k_{\text{eff}}$ on the substituent constant σ^+ at 90°, $C_{\text{H}_2\text{SO}_4} = 56\%$

Figure 2: Fig. 2. Dependence of $\lg k_{\text{eff}}$ on the substituent constant σ^+ at 90°, $C_{\text{H}_2\text{SO}_4} = 56\%$

Let us give a quantitative comparison of the k_{eff} values with the σ^+ values, which take into account direct polar conjugation of the substituent with the reaction center (^{3}). Table 1 gives, as an example, the k_{eff} values for three randomly selected concentrations of sulfuric acid: 30%, 38%, and 56%. The values of the σ^+ constants for triarylcarbinols were calculated by an additive formula of the Jaffé type (^{2}): $\sigma^+ = \Sigma\sigma_i^+$, where σ_i^+ are the values for an individual aryl ring, calculated in turn as the sum of the σ^+ values of the individual substituents in the ring.

In Fig. 2 the data of Table 1 are presented in the coordinates $\lg k_{\text{eff}} - \sigma^+$, where k_{eff} is the rate constant of reduction of the corresponding TAC. From Fig. 2 it is seen that for 56% H_2SO_4 a relationship of type (1) is obeyed. From the slope of the straight line one can find $\rho = +1.71$. For the two other H_2SO_4 concentrations, there is no correlation between the values of $\lg k_{\text{eff}}$ and σ^+. As is evident from the examples given, neither the presence of a correlation between k_{eff} and σ^+ in one case nor its absence in another can serve as a basis for conclusions about the dependence of the reactivity of triarylcarbinols on the nature of the substituent. Apparently, this must always be so when the Hammett-Taft relationship is applied to the observed constants of complex processes, such as the reaction of reduction of TAC by alcohols in acidic media.

Fig. 2. Dependence of $\lg k_{\text{eff}}$ on the substituent constant σ^+ at 90°, $C_{\text{H}_2\text{SO}_4} = 56\%$.

It was shown earlier (^{4,5}) that the reaction of reduction of TAC by iso-C_3H_7OH in an acidic medium is a complex process including two stages:

$$\text{Ph}_3\text{COH} + \text{H}^+ \overset{K}{\rightleftarrows} \text{Ph}_3\text{C}^+ + \text{H}_2\text{O}; \tag{I}$$

$$\text{Ph}_3\text{C}^+ + \text{H:C(CH}_3)_2\text{OH} \xrightarrow{k_{\text{i}}} \text{Ph}_3\text{CH} + (\text{CH}_3)_2\text{C=O} + \text{H}^+, \tag{II}$$

where stage (I) is the rapid and equilibrium ionization of TAC with formation of the carbonium ion; stage (II) is the rate-limiting stage of hydride-ion transfer from the alcohol to the carbonium ion.

It is not difficult to show that the observed effective rate constant for reduction of the TAC carbonium ion (^{4,5})

Fig. 3. Dependence of $\lg K_i$ on the constant σ^+ at 90°

Figure 3: Fig. 3. Dependence of $\lg K_i$ on the constant σ^+ at 90°

Fig. 4. Temperature dependence of ρ_2

Figure 4: Fig. 4. Temperature dependence of ρ_2

$$k_{\text{eff}} = k_i \left(\frac{Kc_0}{1+Kc_0}\right)\left(\frac{1}{1+K_{\text{ROH}}h_0}\right), \tag{2}$$

where k_i is the true rate constant of the rate-limiting stage (II); K and K_{ROH} are equilibrium constants for the ionization reactions of the carbinol and the alcohol in an acidic medium; c_0 and h_0 are the negative antilogarithms of the Deno and Hammett acidity functions, respectively.

Fig. 3. Dependence of $\lg K_i$ on the constant σ^+ at 90°

When comparing the reactivity of a carbinol in this reaction with the nature of the substituent, it seems natural to compare each of the constants entering equation (2)—the true constant k_i and the equilibrium constant K—with the quantity σ^+, which characterizes the substituent.

Table 2

Values of the equilibrium constants K for TPC and its derivatives at 20°

Substituents	H (TPC)	m-CH_3 (DTPC)	n-CH_3 (DTPC)	n-OCH_3 (DAPC)	ρ_1
K	$3.47 \cdot 10^{-7}$	$5.78 \cdot 10^{-7}$	$1.74 \cdot 10^{-5}$	$4.9 \cdot 10^{-2}$	
σ^+	0	−0.066	−0.311	−0.778	−3.25

When $\lg K$ was compared with σ values obtained by different methods, it turned out that the data on the equilibrium constants also correlate with the σ^+ values, i.e., the Taft equation is valid:

$$\lg K/K_0 = \rho\sigma^+. \tag{3}$$

Table 2 presents the values of the equilibrium constants for carbinols with different substituents. The σ^+ values were taken from the work of Brown and Okamoto (3). Practically the same values, $\rho_1 = -3.25$, were obtained in the range from 20 to 80°C.

Fig. 4. Temperature dependence of ρ_2

It may also be shown that dependence (3) describes the ionization data for nine other triarylcarbinols reported in the work of Deno and Schriesheim (9) better than the simple Hammett equation. In this case one obtains $\rho = -3.54$, close to the value ρ_1 found by us. Also differing little from these values is $\rho = -3.97$ for the dissociation reaction of triarylmethyl chlorides in liquid SO_2 (2).

In the same way it was found that the Taft equation is also applicable to the hydride-ion transfer reaction. Figure 3 gives an example of such a correlation for 90°. From the data of Table 3 it follows that, with increasing temperature, ρ_2 increases, and the dependence $\rho = a + \frac{b}{T}$, shown in Fig. 4, is obeyed.

Table 3

Values of the true rate constants of hydride transfer k_h (l/mol • sec) for TPC and its derivatives at different temperatures

Substituent	70°C	80°C	90°C	σ^+
H(TPC)	128.8	335	912	0
m-CH_3(DTPC)	80.0	188.4	451.9	−0.069
n-CH_3(DTPC)	12.4	23.7	48.9	−0.311
n-OCH_3(DATPC)	0.51	0.98	1.57	−0.778
ρ_2	+1.49	+1.56	+1.695	

From the slope of the straight line, the value of the characteristic temperature was found to be
$b = 1.05^\circ$ K.

Combining, according to equation (3), the obtained values of ρ_1 and ρ_2 with equations of type (2), written for any TAC and for the standard substance (TPC), we obtain an expression for the logarithm of the ratio of the effective rate constants

$$\lg k_\text{eff}/k_\text{eff0} = \rho_1\sigma^+ + \rho_2\sigma^+ + \lg \frac{1 + K_0 c_0}{1 + K c_0}. \tag{4}$$

It follows from equation (4) that fulfillment of relation (1) for k_eff depends on the magnitude of the third term, which is a function of the absolute values of the basicity constants of the TAC and of the acidity of the medium. In limiting cases relation (1) will be fulfilled. For example, at $K_0 c_0 \ll 1$ and $K c_0 \ll 1$, $\lg k_\text{eff}/k_\text{eff0} = \sigma^+(\rho_1 + \rho_2)$, which may lead to a decrease of the constant in the series of σ^+ values. In our case this region is bounded above by a sulfuric-acid concentration of about 5% H_2SO_4. At $K_0 c_0 \gg 1$ and $K c_0 \gg 1$, $\lg k_\text{eff}/k_\text{eff0} = \rho_2\sigma^+$. In the series of TAC studied by us, this condition is fulfilled beginning with 46% H_2SO_4.

In the intermediate region, relation (1) for k_eff will not be fulfilled.

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