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Abstract

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ON DETERMINING THE ORDER OF REACTIONS WITH RESPECT TO ACIDITY

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In catalysis by concentrated acids, the degree of conversion of the substrate B into the protonated form BH^+ is determined by the acidity of the medium, i.e., by its ability to donate a proton, and also by the basicity of the substrate:

$$\frac{C_{BH^+}}{C_B} = Kh_0. \tag{1}$$

Here h_0 is the acidity of the medium, and K is the equilibrium constant of the reaction

$$B + H^+ leftarrows BH^+, \tag{2}$$

expressed in terms of activities, characterizing the basicity of B.

According to Hammett ([1]), if the first stage of the reaction is the establishment of equilibrium (2) and the rate-limiting step is the subsequent unimolecular transformation of the protonated form BH^+, then, provided that the degree of protonation is small ($C_{BH^+} \ll C_B$), the observed rate constant k is proportional to h_0.

It is conceivable, however, that cases may occur in which the rate-limiting stage is preceded by the establishment of equilibrium

$$B + 2H^+ leftarrows BH_2^{2+}. \tag{3}$$

In this case k should be proportional to h_0^2 (if h_+—the acidity determined with respect to a singly positively charged base—is proportional to h_0—the acidity with respect to an uncharged base; in what follows, for simplicity, we take $h_+ = h_0$).

Therefore the dependence of k on h_0 is represented by the equation

$$k = \text{const} \cdot h_0^n. \tag{4}$$

Fig. 1

Figure 1: Fig. 1

The exponent n is usually found graphically by plotting $\log k$ against the acidity function $H_0 = -\log h_0$.

In this way, for the decomposition of benzoylformic acid in sulfuric acid it was found that $n = 2$, and the conclusion was drawn that the reaction includes the addition of two protons ([2]).

From the rates of decomposition of other carboxylic acids in sulfuric acid, values of n were obtained that were close to 1, close to 2, and also varied with the acid composition from 1 to 2 and exceeded 2; to explain this, special assumptions concerning the reaction mechanism were put forward ([2]).

We have investigated the kinetics of the decomposition of formic acid into carbon monoxide and water ([3]) in the media H_2SO_4–H_2O (from 80.7 to 98.2% H_2SO_4) and P_2O_5–H_2O (from 72.4 to 83.3% P_2O_5, i.e., in the region of the so-called strong phosphoric acids). Measurements of H_0 of these media were also carried out, including the temperature dependence of H_0 ([4]).

The acidity of the P_2O_5–H_2O system passes through a maximum at a P_2O_5 content of about 80%, in contrast to the H_2SO_4–H_2O system, where the acidit-

monotonically changes with composition (4). This feature of the system P_2O_5—H_2O makes it possible to reveal more clearly the relation between the reaction-rate constant and acidity.

In Fig. 1 the values $-\log k$, extrapolated to 20° by the Arrhenius equation, are presented as a function of $-H_0$.

For decomposition in sulfuric acid, the slope of the straight line corresponds to $n = 1.6$, which does not make it possible to choose between mechanisms corresponding to $n = 1$ and $n = 2$.

The course of the curve for the system P_2O_5—H_2O indicates the inapplicability of equation (4). The same acidity corresponds to substantially different values of the rate constant. It should be assumed[(3)] that the change in the rate constant with the composition of the medium is determined by the superposition of two effects–the influence of acidity and the influence of the nature of the solvent (the Menshutkin effect).

Fig. 1

Without prejudging the question of the number of protons adding to the reacting molecule, and taking as the limiting stage a monomolecular transformation of the protonated form, it is easy, analogously to [(3)], to obtain the expression

$$k = Bh_0^n(x)e^{-A(x)/RT}. \tag{5}$$

Here $h_0(x)$ is the acidity as a function of the acid concentration x; n is the reaction order with respect to acidity; $A(x)$ is the activation energy depending on x, with $A(x) = A_1(x)+\Delta H^0$, where $A_1(x)$ is the activation energy of the limiting stage, and ΔH^0 is the standard change in heat content upon protonation.

The proportionality coefficient $B = B_1 e^{\Delta S^0/R}$, where B_1 is the pre-exponential factor of the rate constant of the limiting stage, and ΔS^0 is the standard change in entropy upon protonation. We assume that B_1, and consequently also B, do not depend on x.

In order to determine n, let us represent h_0 by the equation

$$h_0 = \beta(x) e^{-\alpha(x)/RT}, \tag{6}$$

where $\beta(x)$ and $\alpha(x)$ are certain functions of x.

Equations (5) and (6) give:

$$k = B\beta^n(x) e^{-[A(x)+n\alpha(x)]/RT}. \tag{7}$$

Consequently,

$$k = F(x) e^{-E(x)/RT}, \tag{8}$$

where $F(x)$, the observed pre-exponential factor, and $E(x)$, the observed activation energy, are expressed as follows:

$$F(x) = B\beta^n(x), \tag{9}$$

$$E(x) = A(x) + n\alpha(x). \tag{10}$$

To determine n, it is convenient to use the logarithmic form of equation (9):

$$\log F(x) = \log B + n \log \beta. \tag{11}$$

The quantities $\log \beta$ are calculated from the acidity function and its temperature dependence by means of the equation

$$\log \beta = -H_0 - T \left(\frac{\partial H_0}{\partial T} \right)_x, \tag{12}$$

which follows from (6).

Fig. 2. Plots of $\log F$ versus $\log \beta$ for the systems $H_2SO_4 - H_2O$ and $P_2O_5 - H_2O$.

Figure 2: Fig. 2. Plots of $\log F$ versus $\log \beta$ for the systems $H_2SO_4 - H_2O$ and $P_2O_5 - H_2O$.

Tables 1 and 2 give the values of $\log \beta$ at 20°, calculated from the experimental data ([4]).

Table 1

System H_2SO_4—H_2O

H_2SO_4, %	$\log \beta$	H_2SO_4, %	$\log \beta$
80	5,28	92	6,28
82	5,55	94	6,34
84	5,77	96	6,44
86	5,97	97	6,44
88	6,10	98	6,57
90	6,21	99	6,80

Table 2

System P_2O_5—H_2O

P_2O_5, %	$\log \beta$	P_2O_5, %	$\log \beta$
72,4	0,49	79,0	1,37
73,0	0,56	79,7	1,40
74,0	0,94	81,0	1,10
75,0	1,05	82,0	1,06
76,0	1,14	83,0	0,86
77,0	1,23	83,8	0,74
78,0	1,30	–	–

The quantities $\log \beta$ are somewhat less accurate than H_0. The determination of F from kinetic data is also less accurate than the determination of k. Therefore a graphical plot of $\log F, \log \beta$ gives a greater scatter of points than a plot of $\log k, H_0$.

Fig. 2

In Fig. 2 the points correspond to the experimental data on the decomposition of formic acid ([3]), and the straight lines to the value $n = 1$. Despite the considerable scatter of points in the case of the P_2O_5—H_2O system, it may be concluded that the reaction proceeds through a reversible protonation stage, in

which only one proton is attached to the reacting molecule. This is confirmed by the constancy of the values of B, calculated from equation (5) with $n = 1$ at different x ([3]).

The significant deviation of the value of n from 1, observed in a number of cases when n was determined from equation (4), is apparently a consequence of neglecting the influence of the acid concentration on the activation energy of the reaction.

Determination of n from equation (11) is, in principle, more correct than determination from equation (4), but it imposes considerably higher requirements on the experimental data.

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