SOLVATE SHELL REARRANGEMENTS AND
SOLVATION CORRECTIONS
TO THE BRÖNSTED EQUATION

E. S. Rudakov

Institute of Physical Organic and Coal Chemistry, Donetsk, USSR

Received June 17, 1981
Accepted September 17, 1981

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\[
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The Brönsted equation

\[
k = L K_{\text{HB}} f_{\text{stat}} f_{\text{el}} f_{\text{ster}} f_{\text{solv}}
\]

with statistical, electrostatic, steric and solvation corrections was obtained /1/ for the H\(^+\) transfer reactions in aqueous solutions with variable base B\(^z\)

\[
\text{RH} + \text{OH} \rightarrow \text{RH} \rightarrow \text{RH} + \text{OH} \rightarrow \text{R}^- + \text{HO} \rightarrow \text{HB}^{z+1} \rightarrow \text{R}^- + \text{HO} \rightarrow \text{HB}^{z+1}
\]

(RH are nitroalkanes, ketones, and others) and the usefulness of taking into account the \( f_{\text{stat}} \) and \( f_{\text{el}} \) factors was shown elsewhere /2/.

Let reaction (2) be written in a more general form

\[
a + b \rightarrow c \rightarrow d^* \rightarrow e^* \rightarrow f + g
\]

where \( a, b, \ldots, g \) are the particles in their equilibrium solvate shells, \( c^*, d^*, e^* \) are the particles in rearranged shells and \( d^* \) is the transition state (TS). Concentrations of the respective states will be designated as \( a, b, \ldots, g \). We will restrict ourselves to the case when the rate-determining step is the elementary act (EA) \( c^* \rightarrow e^* \); steps
1, 2, 5, 6 are fast equilibria and the complexes \( c = a \cdot b \) and \( e = f \cdot g \) are of low stability.

The corrections \( f^{\text{solv}} \) are analyzed proceeding from the assumptions \( 3-5 \) that during the process of \( H^+ \) transfer the solvate shell is unchanged. Rearrangements take place before or immediately after the EA (mechanism 3). The Brönsted-Leffler idea of the intermediate position of TS between the initial and final states should be significantly refined, namely, it should be attributed neither to the total reaction \( a + b \rightarrow f + g \) nor to \( c \rightarrow e \), but to \( c, \rightarrow e, \). We have

\[
    k = LK^\beta K_1^{1-\beta} K_2^{1-\beta} K_{5,6}^\beta
\]

where \( k = k/K_1 K_2 \) and \( K^\* = (e^*/c^*) = KK_{5,6}/K_1 K_2 \) are the rate and equilibrium constants of EA; \( k \) and \( K = (fg/ab) \) are the same constants for the reaction \( a + b \rightarrow f + g \); \( K_1 = (c/ab) \), \( K_2 = c^*/c \), \( K_{5,6} = e^*/e \) and \( K_{5,6} = e/fg \) are the equilibrium constants for steps and \( L \) and \( \beta \) are the parameters. These equations were first introduced in Ref. \( 4/ \).

Now assume that the shell rearrangement meets the requirements of MWSR, i.e. the less polar (less solvated) shell rearranges to the more polar state.

The principle of equilibrium solvation of TS (ESTS) has been suggested previously \( 3-5 \) by the author for the \( S_N1 \) reactions \( RX \rightarrow R^+ \ldots X^- \) when the TS is similar to the final state of EA. In this and several other cases the requirements of ESTS and MWSR coincide, namely, the little loss due to the rearrangement of the shell in the low-polar state \( RX \) is compensated by a gain in the solvation energy of about 420 kJ/mol at the end of EA, since the ion pair \( R^+ \ldots X^- \) comes to its equilibrium shell \( 3-5 \). However, situations are possible when the ESTS and MWSR requirements differ, and in terms of better EA thermodynamic conditions, one should prefer MWSR. This can be exemplified by the case of an extremely early TS of the reaction \( RX \rightarrow R^+ \ldots X^- \), when the shell of EA must "fit" \( R^+ \ldots X^- \), i.e. should be nonequilibrium for the TS whose structure is RX.

In the model with a relay molecule of \( H_2O \) in EA \( 1/ \)

\[
    K_1^{1-\beta} K_{5,6}^\beta = f^{\text{el fster}}, \quad K_2^{1-\beta} K_{5,6}^\beta = f^{\text{solv}} \leq 1
\]

\( f^{\text{fster}} \) being independent of \( \beta \) values. Since the nonequilibrium states \( c^* \) and \( e^* \) are less probable than the equilibrium \( c \) and \( e \), from the determination of \( K_2 \) and \( K_{5,6} \) it follows that \( f^{\text{solv}} \leq 1 \) in the range \( 0 \leq \beta \leq 1 \).