NONLINEAR BRÖNSTED RELATIONSHIPS AND THE $\alpha$-EFFECT OF OXIMATE IONS IN ACYL* TRANSFER REACTIONS

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A detailed extrathermodynamic analysis of the behavior of oximate ions ($pK_a = 7-13$) in reactions with various types of substrate was undertaken. For oximate ions with $pK_a \geq 9.0$, irrespective of the nature of the acyl group, the reactivity of the oximes tends toward that of the alcoholate ions, and their $\alpha$-effect disappears. The reason for this is the unfavorable solvation effects of the solvent.

Oximate ions ($\text{Ox}^-$) occupy a special position among the series of typical $\alpha$-nucleophiles. An important role here is played by the fact that antidotes (effective cholinesterase reactivators) were found among the oximes [1]. This property of oximes is connected unambiguously with their $\alpha$-nucleophilic reactivity. Determination of the nature of the $\alpha$-effect therefore remains an urgent and practically important task. Recently [1-3] it was suggested that the nonlinear Brönsted relations for the transfer of the acetyl (I) and diisopropylphosphoryl (II) groups to the oximate ions ($pK_a^{\text{Ox}} = 7-13$), like the "disappearance" of the $\alpha$-effect (at $pK_a \geq 12$), result from the energetically unfavorable solvation effects of the solvent. If this interpretation of the Brönsted relations is correct, such a phenomenon must also be a general relationship in the reactions of oximate ions with substrates of different nature.

In the present work we studied the nucleophilic reactivity of oximes with $pK_a = 7.0-13.0$ toward 2,4-dinitrophenyl toluenesulfonate (III), 4-nitrophenyl toluenesulfonate (IV), 4-nitrophenyl diethyl phosphate (V), and 4-nitrophenyl diethylphosphonate (VI) in water with the addition of ethanol (5-15%) at 25°C. It was compared with the reactivity of "normal" oxygen-containing nucleophiles (aryloxide and alkoxide anions).

*By acyl in the present work we mean not only acetyl but also sulfonyl, phosphoryl, and phosphonyl groups.

Fig. 1. Brønsted relations for the reactions of the oximate (○), alkoxide (●), and aryloxide (*) ions with (I) (a), (II) (b), (III) (c), (IV) (d), (V) (e), and (VI) (f). The dashed lines correspond to the Brønsted relations of the aryloxide and alkoxide ions with the esters (I, III-IV); the data in (a) and (b) were taken from [1, 2, 5, 6].

The numbering of the points corresponds to the nucleophiles: 1) Isonitrosoacetoacetic ester; 2) isonitrosoacetylacetone; 3) pyridine-2-aldoxime methiodide; 4) pyridine-4-aldoxime methiodide; 5) salicylaldoxime; 6) pyridine-3-aldoxime methiodide; 7) pyridine-3'-aldoxime; 8) pyridine-2-aldoxime; 9) benzimidazole-2aldoxime; 10) pyridine-4-aldoxime; 11) 3-bromobenzaldoxime; 12) 4-bromobenzaldoxime; 13) 1-methyl-3-(2-hydroxyiminopropyl)imidazolium bromide; 14) dimethyl glyoxime; 15) 4-methoxybenzaldoxime; 16) 2-hydroxyiminopropyltrimethylammonium bromide; 17) β-furfuraldoxime; 18) imidazole-4(5)-aldoxime; 19) acetaldoxime; 20) cyclohexanone oxime; 21) dimethyl glyoxime; 22) acetoxime; 23) tetrafluoropropanol; 24) propargyl alcohol; 25) choline; 26) glycerol; 27) phenol; 28) hydroxide ion.

The principal aim of the investigation was to establish the scale of variation of the α-effect, the limiting reactivity of the oximes, and the factors responsible for the curvature of the extrathermodynamic Brønsted-type relationships.

The transfer of an acyl group (Ac) to Ox⁻ anions is described by the following scheme:

\[
\text{Ac–OAr} + R\text{–CH=NN=O}^- \rightarrow \text{Ac–O}^-\text{N=CH–R} + \text{OAr}^-.
\]

(1)

where ArO⁻ is 4-nitro- or 2,4-dinitrophenolate ions. The reaction rate with a substrate concentration of 1 M \( (k_H, \text{ sec}^{-1}) \) obeys the equation:

\[
k_H = k_2 K_a \cdot a_{H^-}.
\]

(2)

where \( K_a \) is the acid ionization constant of the oxime, and \( [OxH]_0 \) is its total concentration. Figure 1 shows the Brønsted relations for the reactions of the Ox⁻ anions with (III-VI), the linear sections of which are described by the equations:

\[
\lg k_2^{\text{III}} = (0.50 \pm 0.04) pK_a + (-3.70 \pm 0.30),
\]

\[
n = 5, r = 0.990, S_{\text{gen}} = 0.006,
\]

(3)