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Isokinetic relationship for nucleophilic substitution reactions with a participating thiosulfate ion in aqueous-organic media: a special reaction mechanism

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For 72 nucleophilic substitution reactions at a saturated carbon atom with the participation of the $S_2O_3^{2-}$ anion in aqueous-organic media, an isokinetic relationship with T_{iso} = 1130 K and lg k_{iso} = 5.949 was found.

For a series reactions, the isokinetic relationship (IKR) reflects a linear relationship between the activation energy E_a and the logarithm of the pre-exponential factor A of the Arrhenius equation.[1] A search of IKR and systematization of kinetic data on this basis represent an urgent problem. These IKR, which are applicable to a wide variety of reactions, are very useful. They can be applied to the quantitative prediction of the reactivity of chemical compounds using computer expert systems.[2] The existence of an IKR for a series of reactions suggests that they occur by identical mechanisms.[3] Therefore, statistically significant deviations from a general IKR for particular reactions indicate that they occur by a special mechanism.

Previously, the fulfilment of a general IKR[4,5] for nucleophilic substitution reactions at a saturated carbon atom with the participation of anionic nucleophiles N^{-z} (z is the charge of the anion) was established,

$$YCH_2X + N^{-z} = YCH_2N^{-z+1} + X^-, \qquad (1)$$

where X and X^- are the leaving group and its anion, respectively: Y is the substituent at a saturated carbon atom. The rate constants k (dm^3 mol^{-1} s^{-1}) of 165 reactions like (1) in proton-donor and polar aprotic solvents and their mixtures at various temperatures T were described by a general IKR with the parameters T_{iso} = 6103 K and lg k_{iso} = 10.402.[5]

It was found that this IKR is applicable to many reactions like (1) in different solvents. The exception is provided by reactions with the participation of the $S_2O_3^{2-}$ anion in the mixtures of water with organic solvents. In contrast to reactions (1) with the $S_2O_3^{2-}$ anion in water, which exhibit no special behaviour,[4] the above reactions are not described by the general IKR.[5] In this work, the applicability of IKR to nucleophilic replacement reactions at saturated carbon with the participation of the $S_2O_3^{2-}$ anion in mixed solvents is analysed.

If an IKR is fulfilled for a series of reactions, the relations lg $k = f(1/T)$ for the members of this series should statistically satisfy the equations of straight lines that pass through an isokinetic point with the coordinates lg k_{iso}, $1/(2.303RT_{iso})$[3]

$$\lg k - \lg k_{iso} = -E_{iso}[(2.303RT)^{-1} - (2.303RT_{iso})^{-1}] \qquad (2)$$

According to equation (2), each member of the series has its own isokinetic activation parameters E_{iso} and $\lg A_{iso} = \lg k_{iso} + E_{iso}/(2.303RT_{iso})$.

The values of T_{iso} and lg k_{iso} and the array of E_{iso} and lg A_{iso} values for the series of reactions are calculated using the least-squares method by varying the values of T_{iso} and lg k_{iso} until the minimum sum $S = \sum(\lg k - \lg k')^2$ was achieved. Here, lg k' are the logarithms of rate constants calculated for the members of the series by equations (3)

$$\lg k' = \lg A_{iso} - E_{iso}(2.303RT)^{-1} \qquad (3)$$

The calculations were performed using the ISOKIN program.[4] The program made it possible to calculate the values of E_{iso} and lg A_{iso} at fixed values of T_{iso} and lg k_{iso}; this calculation is necessary for testing the applicability of IKR to different kinetic data.

In the calculations of IKR, rate constants should be corrected for the statistical factors F,[4,5] which take into account the number of identical nucleophilic atoms in anions and the number of identical reaction centres in substrates. In this work, the statistical factor $F = 1$ was used for the $S_2O_3^{2-}$ anion because one negatively charged sulfur atom of the $S–S^-$ bond participates in the reaction.[6]

An analysis of the rate constants of reactions (1) with the participation of the $S_2O_3^{2-}$ anion in aqueous-organic mixtures[6–10] demonstrated that cannot be described by a general IKR.[5] The calculation of E_{iso} for these reactions using the parameters T_{iso}, and lg k_{iso} from ref. 5 gives the values of E_{iso} higher than experimental E_a by 12–17 kJ mol^{-1}. In contrast, the values of lg k for reactions (1) with the $S_2O_3^{2-}$ anion in water were described by a general IKR.[4]

The values of lg k (n = 234) were analysed for 72 nucleophilic substitution reactions at a saturated carbon atom with the participation of the $S_2O_3^{2-}$ anion in the mixtures of water with ethanol,[6–9] acetone,[9,10] dimethyl sulfoxide,[10] and dioxane,[10] as well as in the mixtures of water (40 vol%) with dimethoxyethane,[9] diglyme[9] and butyrolactone.[9] The water content of the mixtures was lower than 64 wt%. Substituted benzyl chlorides, alkyl chlorides and alkyl bromides participated in reactions. For each member of a series, the number of k values at different temperatures was no lower than 3, and the temperature range in which they were measured was not narrower than 20 K.

The test series was described by an IKR with the parameters T_{iso} = 1130 K and lg k_{iso} = 5.949 at $s = [S/(n-2)]^{0.5}$, which is equal to 0.025. This fact is indicative of the occurrence of a special mechanism for analysed reactions. The quality of the obtained IKR is characterised by a regression between the values of lg k included in the series and the values of lg k' calculated by equation (3) at a minimum S for all members of the series

$$\lg k = (1.000\pm0.002)\lg k' + (0.000\pm0.005)$$
$$n = 234,\ s = 0.025,\ r = 0.9995$$

The regression coefficient equal to 1, the absence of a constant from the equation, a low value of s and a high value of r confirm the fulfilment of IKR for reactions (1) with the participation of the $S_2O_3^{2-}$ anion in the test aqueous-organic media. As expected, the values of lg k for similar reactions in water[4] cannot be described by the found IKR.

The following compensation relationship between the parameters E_{iso} and lg A_{iso} for the members of a test series was calculated:

$$E_{iso} = (21.639\pm0.003)\lg A_{iso} - (128.731\pm0.024)$$
$$n = 72,\ r = 0.9999,\ s = 0.007$$

A similar compensation relationship between Arrhenius parameters (E_a and lg A) for the members of a test series is approximate because the parameters E_a and lg A are characterised by high values of s.

$$E_a = (7.69\pm0.68)\lg A - (4.1\pm6.2)$$
$$n = 72,\ r = 0.804,\ s = 4.6$$

The values of lg k for the reactions of substituted benzyl chlorides with the $S_2O_3^{2-}$ ion in the water–*N*-methylacetamide system (60 vol%, permittivity D = 101)[9] are adequately described by a general IKR;[5] therefore, they are not included in the analysed series.

As mentioned above, the observed values of E_a in these media for the test reactions are lower by 12–17 kJ mol^{-1} than those estimated by a general IKR. This fact can be explained by the occurrence of a catalytic reaction path.

In the water–ethanol (44 wt%) system, sodium thiosulfate forms ion pairs with smaller radii in comparison with ion pairs in water,[11] namely, contact ion pairs. Probably, they are also formed in other aqueous-organic media with permittivities lower than that of water, in which solvent-separated ion pairs are formed.[11]

It should be noted that in the calculation of a general IKR reactions in aqueous-organic media with the participation of singly charged anions, which form solvent-separated ion pairs in these media,[12] were included in the test series.[5] On this basis, it is possible to assume that the formation of contact ion pairs by sodium thiosulfate in aqueous-organic media with low values of D is promoted by the large charge (–2) of $S_2O_3^{2-}$ anions. Probably, the structure of the contact ion pairs of sodium thiosulfate allows the interaction of the cation of an ion pair with the leaving anion to cause the electrophilic catalysis of reactions.

The test reactions may occur by two parallel mechanisms. In this connection, it is interesting to note the kinetic data for the reactions with the participation of the $S_2O_3^{2-}$ anion in the water–acetonitrile (60 vol%, $D = 52.3$) system.[9] The observed values of E_a for reactions in this system are much higher than E_{iso} calculated by the IKR for the test series (this system was not included in the calculation of IKR). This system has a high value of D, and solvent-separated ion pairs reacting by the general mechanism can prevail here.

The values of E_a for nucleophilic substitution reactions at a saturated carbon atom with the participation of the $S_2O_3^{2-}$ anion in aqueous-organic media are reduced. This fact can be explained by the ability of cations in the contact ion pairs of sodium thiosulfate to electrophilic catalysis. It is believed that nucleophilic substitution reactions with the participation of other doubly and multiply charged anions in similar media can occur by analogous mechanisms.

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