Isokinetic relationships for nucleophilic substitution at the saturated carbon atom. Reactions with anions in the gas phase and various solvents

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Isokinetic relationship (IKR) with the parameters $T_{\rm iso}$ = 6103 K and $\log k_{\rm iso}$ = 10.402 is applicable to the rate constants for 165 reactions of nucleophilic substitution at the saturated carbon atom involving anionic nucleophiles in proton-donor and polar aprotic solvents and their mixtures. For analogous reactions in the gas phase proceeding *via* a specific mechanism, IKR is obtained with the parameters $T_{\rm iso}$ = 1505 K and $\log k_{\rm iso}$ = 9.972, which is applicable to the reactions occurring under various pressures of an inert gas.

Key words: nucleophilic substitution, anionic nucleophiles, rate constants, isokinetic relationship, activation parameters, influence of solvents, reactions in the gas phase.

An isokinetic relationship (IKR) reflecting a linear correlation between the enthalpy and entropy components of the free activation energies[1] in a series of reactions is commonly used to find the general character of the mechanism of the reactions under study.[2,3] Other possibilities of the application of IKR are poorly studied. It is known that the isokinetic temperature $T_{\rm iso}$ depends on the average height of the potential barrier of the reactions that compose a series and can serve as a basis for the quantitative classification of reaction mechanisms.[2,4]

It is established[5] that IKRs are fulfilled for nucleophilic substitution in aqueous solutions at the saturated carbon atom. These reactions occur *via* the S_N2 mechanism involving the anionic nucleophiles N^{z-} (z is the charge of the anion)

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

where X is the eliminated (in the form of the anion X^-) group, and Y is the substituent at the saturated carbon atom. As has been shown by some preliminary tests,[5] the isokinetic parameters for 60 reactions of type (1) in water $T_{\rm iso}$ = 6145 K and $\log k_{\rm iso}$ = 10.622 describe the temperature relations of the rate constants of reactions (1) in polar organic solvents with an appropriate accuracy. However, for reactions (1) in the gas phase these parameters do not completely agree with the temperature relations of the rate constants. In this work, with the purpose of revealing the possibility of the single IKR for reactions (1) in solvents with different polarities, we performed combined statistical analysis of the kinetic data for reactions (1) in water[5] and various solvents.[6—21]

Reactions (1) in the gas phase occur *via* a special mechanism including the intermediate formation of an ion-dipole complex of the nucleophilic anion and polar reactant and a similar complex of the formed anion and reaction product. Since the mechanism is complicated, both positive and negative activation energies are possible.[22] Similar reactions have been under extensive study in recent years.[23] Therefore, we considered the possibility of IKR fulfillment for several reactions (1) in the gas phase, for which the temperature relations of the rate constants have been found recently.[24,25]

The applicability of IKR for a reaction series is often examined for small (by the number of members) selections,[3] and the IKR parameters determined under these conditions ($T_{\rm iso}$, isokinetic rate constant $k_{\rm iso}$ at $T = T_{\rm iso}$) can depend strongly on the composition of the selections. For a more exact calculation of $T_{\rm iso}$ and $k_{\rm iso}$, one should use sufficiently broad (by the number of members and temperature intervals) selections, which is also reasonable for the determination of the applicability limits of IKR, establishment of general reaction mechanisms, and elucidation of special mechanisms. When IKR are fulfilled, the presence or absence of systematic errors of the kinetic data from specific works and the real level of random errors in the analyzed series of parameters can objectively be evaluated. Therefore, we performed the combined statistical analysis of the kinetic data obtained by independent authors for reactions with the general mechanism (1).

Calculation procedure

The examined reaction series under the fulfillment of IKR is characterized by two parameters common for all members of

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the series, *viz.*, $T_{\rm iso}$ and $k_{\rm iso}$. These parameters determine the coordinates of the isokinetic point $\log k_{\rm iso}$, $1/(2.303RT_{\rm iso})$, when calculation is performed by the Arrhenius equation $\log k = \log A - E_a/(2.303RT)$, where k is the experimental rate constant (at the temperature T), A is the pre-exponential factor, E_a is the activation energy, and R is the gas constant. The plots of $\log k$ *vs.* T^{-1} for the members of the series in the case of IKR fulfillment should statistically satisfy the linear equations that pass through the isokinetic point[1—3]

$$\log k - \log k_{\rm iso} = -E_{\rm iso}[(2.303RT)^{-1} - (2.303RT_{\rm iso})^{-1}]. \quad (2)$$

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

The parameters $T_{\rm iso}$ and $\log k_{\rm iso}$ and the array of $E_{\rm iso}$ and $\log A_{\rm iso}$ for the reaction series were calculated by the least-squares method, varying the $T_{\rm iso}$ and $\log k_{\rm iso}$ values until the minimum of the sum $S = \Sigma(\log k - \log k')^2$ was achieved, where $\log k'$ are the logarithms of rate constants calculated for the members of the series from equations in the form

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

Calculations were performed using the ISOKIN program,[5] which makes it possible to calculate, along with $T_{\rm iso}$ and $\log k_{\rm iso}$, the least-squares parameters of the Arrhenius equations and similar isokinetic values ($E_{\rm iso}$ and $\log A_{\rm iso}$) for the members of the series and the standard deviations s of the corresponding values. The program also allows one to estimate the parameters and statistical indicators (the correlation coefficient r and the s value) of the regression between the $\log k$ values included in the calculation and $\log k'$ calculated by Eq. (3) at the minimum S for all members of the series.

The considered series consists of reactions (1) with mono- and polyatomic anions and, hence, we used in calculations the k values corrected by the division into the statistical factors F according to the previously published procedure.[5] For the AcO^- and $PhCO_2^-$ ions, we accepted $F = 2$, and for ArO^-, $PhCH_2O^-$, and PhS^-, $F = 1$. Some reactants had two or three identical electrophilic centers, and for them the additional $F = 2$ or 3 were taken into account.

We included in the series only the data in which the number of k at different T was at least three and the T interval, in which k were defined, was at least 15 °C. The dimensionality of k for the gas phase reactions (cm^3 molecule^{-1} s^{-1}) was recalculated to that accepted in this work by the formula 1 L mol^{-1} s^{-1} = $6.02 \cdot 10^{20}$ cm^3 molecule^{-1} s^{-1}.

Results and Discussion

To solve the problem of the applicability of IKR obtained for reactions in aqueous solutions[5] to similar reactions in other media, we need a statistical analysis of the fulfillment of the general IKR on the selection, including solvents differing in properties. That is why the examined series[5] of reactions was extended by the inclusion of reactions (1) in various proton-donor (alcohols), polar aprotic (Me_2SO, Me_2CO, $MeNO_2$, DMF), and mixed solvents.[6—21] The number of $\log k$ values included into the statistical processing (n) increased almost threefold, which made it possible to reliably check the general IKR in various solvents. The performed calculation suggests that $\log k$ included in the selection at different T satisfies the single IKR for all solvents with $s = [S_{\rm min}/(n - 2)]^{0.5}$ equal to 0.051, which corresponds to the reproducibility level of $\log k$ found by independent authors.[5]

The isokinetic parameters obtained for the considered series (n = 653, 165 reactions in 10 media), *viz.*, $T_{\rm iso}$ = 6103 K and $\log k_{\rm iso}$ = 10.402, agree with those determined previously[5] for reactions (1) in water. They were used in the calculation of $E_{\rm iso}$ and $\log A_{\rm iso}$ for the reactions included in the series and partially (for the reactions considered for the first time) presented in Table 1. The $E_{\rm iso}$ and $\log A_{\rm iso}$ values for the reactions in water are not presented in Table 1 because they are close to those found previously[5] ($E_{\rm iso}'$ and $\log A_{\rm iso}'$), and the corresponding new values can be estimated by the formulas $E_{\rm iso} = E_{\rm iso}' - (1.36\pm0.12)$ and $\log A_{\rm iso} = \log A_{\rm iso}' - (0.226\pm0.001)$.

The quality of the obtained IKR is characterized by regression between $\log k$ included in the selection and $\log k'$ for the analyzed reaction series, which were calculated by Eq. (3) at the minimum S:

$$\log k = (1.000\pm0.002)\lg k' + (0.000\pm0.006)$$
$$(n = 653,\ s = 0.051,\ r = 0.999).$$

The regression coefficient equal to unity, the absence of the constant from the equation, a low value of s, and high r confirm the fulfillment of IKR for reactions (1) in the considered solvents. Since the IKR between E_a and $E_{\rm iso}$ exists, the correlation $E_a = (0.998\pm0.005)E_{\rm iso}$ describes all members of the series (n = 165, s = 5.9, r = 0.998). A positive $T_{\rm iso}$ value indicates a compensation effect[1] between the parameters $E_{\rm iso}$ and $\log A_{\rm iso}$ for the members of the series.

The interval of changing $E_{\rm iso}$ in the considered series of reactions (1) is 59 kJ mol^{-1}, which corresponds to the range of k variation at 298 K by more than 10 orders of magnitude. However, a slight change in $\log A_{\rm iso}$ in the series (±0.253) indicates the prevailing effect of the enthalpy component of the free activation energy on the reaction rate (1). Due to this, a change in the nature of anions and replaced groups at the reaction center mainly affects E_a and $E_{\rm iso}$, whereas $\log A$ and $\log A_{\rm iso}$ slightly depend on the structure of the reactants and the solvent nature (see Table 1). It has recently been shown[26] that the solvation energy of the transition state mainly contributes to the activation energy of ion-molecular reactions that occur in solutions *via* the S_N2 mechanism.

The reactions of nucleophilic substitution at the saturated carbon atom occurring in solutions *via* the single-step S_N2 mechanism (1) in the gas phase include the intermediate formation of two ion-molecular complexes, one of which consists of the reactants, and the other of which is formed from the reaction products. For this mechanism, the effective rate constant is complicated: $k = k_1k_3/(k_2+k_3)$. The constants k_1, k_2, and k_3 correspond to the formation of a complex between the reactants, its inverse dissociation, and its transformation into a complex between the products, respectively. The latter then dissociates to the reaction products. It is difficult to

Table 1. Activation parameters of reactions (1) in various solvents calculated by the Arrhenius equation and using the isokinetic relationship (T_{iso} = 6103 K, logk_{iso} = 10.402)

Reaction	Solvent	Refs.	E_a /kJ mol^{-1}	log$A$	E_{iso} /kJ mol^{-1}	logA_{iso}
MeCl + SCN$^-$	MeOH	6	96.19±0.50	10.99±0.08	97.86±0.06	11.239±0.001
MeCl + SCN$^-$	DMF	6	80.77±0.45	9.68±0.07	90.73±0.36	11.178±0.003
EtCl + HO$^-$	EtOH	7	97.49±0.77	10.99±0.12	99.16±0.06	11.251±0.000
$C_6H_{13}Cl$ + Cl^{-a}	DMSO	8	96.60±1.63	11.97±0.26	91.59±0.17	11.186±0.001
sec-$C_6H_{13}Cl$ + Cl^{-a}	DMSO	8	102.16±2.27	11.49±0.34	100.61±0.09	11.263±0.001
C_6H_{13}—Cl-3 + Cl^{-a}	DMSO	8	104.39±1.44	11.88±0.21	100.22±0.11	11.260±0.001
cyclo-PrCl + Cl^{-a}	DMSO	9	100.03±0.81	11.49±0.12	98.41±0.07	11.244±0.001
cyclo-$C_6H_{13}Cl$ + Cl^{-a}	DMSO	9	118.35±2.59	12.57±0.34	108.99±0.22	11.335±0.002
cyclo-$C_7H_{15}Cl$ + Cl^{-a}	DMSO	9	101.23±0.60	11.39±0.09	100.32±0.05	11.261±0.000
cyclo-$C_8H_{17}Cl$ + Cl^{-a}	DMSO	9	110.62±1.08	12.07±0.16	105.34±0.21	11.304±0.002
$PhCH_2Cl$ + N_3^-	MeOH	10	84.37±3.67	10.19±0.54	91.05±0.24	11.181±0.002
MeBr + Cl$^-$	DMF	11	75.09±2.15	12.77±0.42	65.91±0.18	10.966±0.002
EtBr + Cl$^-$	DMF	11	79.78±2.34	12.02±0.42	74.34±0.10	11.038±0.001
PrBr + Cl$^-$	DMF	11	75.22±2.95	10.99±0.53	75.56±0.09	11.049±0.001
Pr^{i}Br + Cl$^-$	DMF	11	89.40±1.06	11.95±0.17	84.41±0.09	11.124±0.001
Bu^{i}Br + Cl$^-$	DMF	11	82.01±1.00	10.92±0.17	83.16±0.04	11.114±0.000
neo-C_5H_{11} + Cl$^-$	DMF	11	110.04±1.16	12.12±0.16	104.04±0.09	11.292±0.001
MeBr + N_3^-	DMF	6	69.44±0.80	11.62±0.15	66.07±0.14	10.967±0.001
MeBr + I$^-$	MeOH	12	75.21±0.55	10.16±0.09	80.62±0.12	11.092±0.001
MeBr + I$^-$	Me_2CO	13	69.90±0.82	11.69±0.16	66.13±0.06	10.968±0.001
EtBr + I$^-$	Me_2CO	13	84.39±4.41	11.96±0.76	79.28±0.18	11.080±0.002
PrBr + I$^-$	Me_2CO	13	80.67±1.05	11.28±0.18	79.49±0.03	11.082±0.000
Pr^{i}Br + I$^-$	Me_2CO	13	85.89±0.37	10.15±0.06	92.31±0.07	11.192±0.001
Bu^{i}Br + I$^-$	Me_2CO	13	84.30±0.59	10.55±0.10	88.07±0.05	11.156±0.000
Bu^{t}Br + I$^-$	Me_2CO	13	91.03±1.34	9.96±0.22	98.92±0.15	11.249±0.001
neo-C_5H_{11} + I$^-$	Me_2CO	13	101.63±0.16	10.36±0.02	108.16±0.12	11.328±0.001
MeBr + SCN$^-$	MeOH	6	85.54±3.63	11.38±0.61	84.00±0.15	11.121±0.001
EtBr + HO$^-$	EtOH	7	90.12±0.47	11.38±0.08	88.79±0.05	11.162±0.000
EtBr + PhS$^-$	MeOH	14	78.09±0.50	11.51±0.09	75.53±0.10	11.048±0.001
PrBr + PhS$^-$	MeOH	14	76.32±0.25	11.00±0.05	76.61±0.01	11.058±0.000
Pr^{i}Br + PhS$^-$	MeOH	10	82.99±3.25	10.76±0.49	85.42±0.14	11.133±0.001
BuBr + PhS$^-$	MeOH	14	76.25±0.27	11.02±0.05	76.46±0.01	11.056±0.000
BuBr + PhS$^-$	DMF	10	51.92±3.39	10.49±0.73	53.64±0.09	10.861±0.001
FCH_2CH_2Br + PhS$^-$	MeOH	14	83.65±0.65	11.60±0.12	80.83±0.11	11.094±0.001
$ClCH_2CH_2Br$ + PhS$^-$	MeOH	14	81.82±0.42	11.33±0.08	80.47±0.05	11.091±0.000
$BrCH_2CH_2Br$ + PhS$^-$	MeOH	14	80.90±0.31	11.12±0.06	80.76±0.01	11.093±0.000
Pr^{i}Br + N_3^-	MeOH	10	98.73±2.81	11.57±0.41	96.36±0.08	11.227±0.001
Bu^{i}Br + N_3^-	DMF	11	73.64±0.58	9.66±0.10	82.07±0.18	11.104±0.002
Bu^{i}Br + N_3^-	MeOH	10	96.79±2.67	10.28±0.38	103.97±0.17	11.292±0.001
4-$NO_2C_6H_4CH_2Br$ + N_3^-	DMF	10	57.17±3.38	11.14±0.73	55.95±0.09	10.881±0.001
$C_6H_{13}Br$ + Br^{-a}	DMSO	8	79.43±1.15	10.99±0.20	80.00±0.04	11.087±0.000
sec-$C_6H_{13}Br$ + Br^{-a}	DMSO	8	82.71±2.57	10.20±0.41	88.73±0.15	11.161±0.001
3-Br—C_6H_{13} + Br^{-a}	DMSO	8	85.22±10.60	10.76±1.69	87.69±0.31	11.152±0.003
PrBr + Br^{-a}	H_2O—Me_2CO^b	15	77.63±2.72	10.12±0.46	83.51±0.33	11.116±0.003
Pr^{i}Br + Br^{-a}	H_2O—Me_2CO^b	15	97.77±2.27	12.20±0.37	91.60±0.20	11.186±0.002
Bu^{i}Br + Br^{-a}	H_2O—Me_2CO^b	15	86.26±3.67	10.37±0.61	91.19±0.20	11.183±0.002
MeI + SCN$^-$	MeOH	6	79.68±3.78	10.68±0.63	82.27±0.15	11.106±0.001
MeI + SCN$^-$	DMF	6	61.47±2.71	9.60±0.48	69.24±0.32	10.995±0.003
MeI + Br$^-$	MeOH	12	89.65±1.08	11.61±0.18	86.91±0.09	11.146±0.001
MeI + AcO$^-$	MeOH	16	99.82±2.19	11.20±0.31	100.24±0.11	11.260±0.001
MeI + $PhCO_2^-$	MeOH	16	95.00±2.85	10.57±0.42	99.59±0.19	11.254±0.002
MeI + PhO$^-$	MeOH	16	92.71±0.41	11.99±0.06	87.40±0.13	11.150±0.001
MeI + 4-$NO_2C_6H_4O^-$	MeOH	16	92.61±0.88	10.74±0.13	95.82±0.12	11.222±0.001
MeI + 2,4-$(NO_2)_2C_6H_4O^-$	MeOH	16	102.81±1.15	10.96±0.17	105.07±0.08	11.301±0.001
MeI + 4-$NO_2C_6H_4O^-$	DMF	16	62.02±5.84	8.99±1.05	73.37±0.47	11.030±0.004
MeI + 2,4-$(NO_2)_2C_6H_4O^-$	DMF	16	70.44±8.64	8.67±1.41	85.50±0.65	11.134±0.006
BuI + Cl$^-$	MeOH	10	95.28±0.98	10.52±0.15	100.09±0.26	11.259±0.002
BuI + Br$^-$	MeOH	10	96.86±7.89	11.36±1.13	95.92±0.23	11.223±0.002

(*to be continued*)

Table 1 (*continued*)

Reaction	Solvent	Refs.	E_a /kJ mol^{-1}	log$A$	E_{iso} /kJ mol^{-1}	logA_{iso}
BuI + SCN$^-$	MeOH	10	82.48±5.30	9.83±0.79	91.60±0.36	11.186±0.003
BuI + N_3^-	MeOH	10	90.45±1.56	10.78±0.23	93.24±0.11	11.200±0.001
BuI + NO_2^-	MeOH	10	90.31±2.36	10.25±0.34	97.10±0.15	11.233±0.001
MeI + $PhCH_2O^-$	EtOH	17	85.78±0.77	12.21±0.14	79.58±0.20	11.083±0.002
EtI + $PhCH_2O^-$	EtOH	17	91.79±0.27	12.19±0.05	85.56±0.14	11.134±0.001
PrI + $PhCH_2O^-$	EtOH	17	91.29±0.51	11.69±0.08	88.04±0.07	11.155±0.001
Pr^iI + $PhCH_2O^-$	EtOH	17	89.56±0.37	11.17±0.06	89.53±0.01	11.168±0.000
BuI + $PhCH_2O^-$	EtOH	17	90.33±0.39	11.40±0.06	88.92±0.03	11.163±0.000
Bu^iI + $PhCH_2O^-$	EtOH	17	89.77±0.73	11.41±0.12	88.23±0.04	11.157±0.000
iso-C_5H_{11} + $PhCH_2O^-$	EtOH	17	90.25±3.11	11.10±0.51	90.70±0.09	11.178±0.001
sec-C_5H_{11} + $PhCH_2O^-$	EtOH	17	90.90±0.05	11.64±0.01	87.94±0.06	11.155±0.001
$C_7H_{15}I$ + $PhCH_2O^-$	EtOH	17	90.15±0.69	11.37±0.11	88.90±0.03	11.163±0.000
$C_8H_{17}I$ + $PhCH_2O^-$	EtOH	17	90.33±0.39	11.39±0.06	88.98±0.03	11.164±0.000
sec-$C_8H_{17}I$ + $PhCH_2O^-$	EtOH	17	91.11±0.56	11.56±0.09	88.69±0.05	11.161±0.000
$C_{16}H_{33}I$ + $PhCH_2O^-$	EtOH	17	88.76±0.44	11.13±0.07	88.95±0.01	11.163±0.000
MeI + CN$^-$	H_2O—EtOH^c	18	76.81±1.57	10.78±0.27	78.48±0.07	11.074±0.001
EtI + CN$^-$	H_2O—EtOH^c	18	86.45±9.64	11.90±1.67	81.87±0.35	11.103±0.003
PrI + CN$^-$	H_2O—EtOH^c	18	79.87±4.47	10.60±0.78	82.79±0.17	11.111±0.001
MeI + CN$^-$	H_2O	18	79.80±1.35	10.70±0.23	82.14±0.10	11.105±0.001
EtI + HO$^-$	EtOH	7	90.33±0.41	11.73±0.07	86.76±0.10	11.144±0.001
EtI + OH$^-$	H_2O—DMSO^d	19	66.02±0.08	10.19±0.01	70.57±0.05	11.006±0.000
PrI + OH$^-$	H_2O—DMSO^d	19	68.89±0.38	10.38±0.07	72.49±0.04	11.022±0.000
BuI + OH$^-$	H_2O—DMSO^d	19	69.52±0.61	10.39±0.11	73.04±0.04	11.027±0.000
$C_5H_{11}I$ + OH$^-$	H_2O—DMSO^d	19	67.88±0.68	10.11±0.12	72.97±0.06	11.026±0.001
$C_6H_{13}I$ + OH$^-$	H_2O—DMSO^d	19	73.45±0.32	11.10±0.06	73.07±0.01	11.027±0.000
$C_7H_{15}I$ + OH$^-$	H_2O—DMSO^d	19	68.58±0.63	10.19±0.11	73.22±0.06	11.029±0.000
$C_8H_{17}I$ + OH$^-$	H_2O—DMSO^d	19	68.25±0.32	10.14±0.06	73.18±0.06	11.028±0.000
$C_9H_{19}I$ + OH$^-$	H_2O—DMSO^d	19	67.96±0.85	10.08±0.15	73.22±0.06	11.029±0.001
$C_{10}H_{21}I$ + OH$^-$	H_2O—DMSO^d	19	72.99±7.72	10.94±1.39	73.48±0.13	11.031±0.001
$MeOSO_2Me$ + Cl$^-$	$MeNO_2$	20	83.09±3.12	11.96±0.52	77.79±0.24	11.068±0.002
$MeOSO_2Me$ + Br$^-$	$MeNO_2$	20	78.95±1.56	10.99±0.26	79.52±0.06	11.083±0.001
$MeOSO_2Me$ + I$^-$	$MeNO_2$	20	81.75±1.66	11.35±0.28	80.22±0.09	11.088±0.001
MeOTs + N_3^-	MeOH	10	65.98±2.98	7.94±0.49	85.61±0.95	11.135±0.008
MeOTs + N_3^-	DMF	10	57.24±1.99	8.39±0.36	71.66±0.24	11.015±0.002
MeOTs + SCN$^-$	MeOH	10	74.41±2.25	9.22±0.36	86.33±0.44	11.141±0.004
MeOTs + SCN$^-$	DMF	10	84.15±1.83	11.62±0.30	80.98±0.11	11.095±0.001
$C_6H_{13}OTs$ + Cl$^-$	DMSO	21	87.72±0.46	12.33±0.08	80.51±0.14	11.091±0.001
$C_6H_{13}OTs$ + Cl$^-$	MeOH	21	104.49±0.01	12.36±0.00	98.02±0.13	11.241±0.001
$C_6H_{13}OTs$ + Br$^-$	DMSO	21	88.57±0.77	12.02±0.13	83.32±0.11	11.115±0.001
$C_6H_{13}OTs$ + Br$^-$	MeOH	21	98.34±0.11	11.80±0.02	94.93±0.07	11.214±0.001
$C_6H_{13}OTs$ + I$^-$	DMSO	21	90.13±0.23	11.77±0.04	86.35±0.07	11.141±0.001
$C_6H_{13}OTs$ + I$^-$	MeOH	21	96.21±1.17	12.02±0.20	91.34±0.10	11.184±0.001
$C_6H_{13}OTs$ + N_3^-	DMSO	21	81.12±0.03	11.36±0.00	79.52±0.03	11.083±0.000
$C_6H_{13}OTs$ + N_3^-	MeOH	21	91.21±0.62	11.13±0.11	91.53±0.01	11.185±0.000
$C_6H_{13}OTs$ + SCN$^-$	DMSO	21	86.55±0.68	10.48±0.12	90.59±0.08	11.177±0.001
$C_6H_{13}OTs$ + SCN$^-$	MeOH	21	85.52±0.55	9.95±0.10	92.75±0.15	11.196±0.001
$(MeO)_3PO$ + N_3^-	MeOH	10	102.16±6.33	10.52±0.92	107.68±0.18	11.324±0.002

[a] Isotope exchange reaction.

[b] Concentration of Me_2CO is 68.9 mol.%.

[c] Concentration of EtOH is 50% (v/v).

[d] Concentration of DMSO is 90% (v/v).

determine the rate constants of reactions (1) in the gas phase at different temperatures. Reliable methods for the solution of this problem have been developed only recently. Therefore, the kinetic data obtained by the temperature variation are scarce.

The analyzed series of reactions (1) in the gas phase contains log$k$ (n = 70) determined[27,28] in a wide temperature range (>110 K). The rate constants depend on the presence of inert gases (CH_4, N_2) and were obtained at two gas pressures. Our calculation showed the fulfill-

Table 2. Activation parameters of reactions (1) in the gas phase calculated by the Arrhenius equation and using the isokinetic relationship parameters (T_{iso} = 1505 K, $\log k_{iso}$ = 9.972)

Reaction	p*/Torr	Refs.	E_a /kJ mol^{-1}	$\log A$	E_{iso} /kJ mol^{-1}	$\log A_{iso}$
MeBr + Cl$^-$	3	24	−2.05±0.47	9.87±0.07	−1.78±0.06	9.911±0.002
MeBr + Cl$^-$	640	24	−5.96±0.10	9.50±0.01	−3.61±0.15	9.847±0.005
EtBr + Cl$^-$	3	24	4.10±0.60	10.37±0.09	1.85±0.17	10.036±0.006
EtBr + Cl$^-$	640	24	3.46±0.51	10.29±0.07	1.75±0.15	10.033±0.005
Pr^{i}Br + Cl$^-$	640	25	13.45±0.49**	10.42±0.07	13.61±0.08	10.445±0.003
BuBr + Cl$^-$	3	24	−0.25±0.73	10.01±0.11	−0.63±0.10	9.951±0.003
BuBr + Cl$^-$	640	24	−2.15±0.60	9.84±0.09	−1.69±0.08	9.914±0.003

* Inert gas pressure in the reaction system.

** Previously[25] presented E_a = 5.86 kJ mol^{-1} contains a calculation error.

ment of the general IKR for the reactions studied at different inert gas pressures with s = 0.043 and the isokinetic parameters T_{iso} = 1505 K and $\log k_{iso}$ = 9.972. The E_{iso} and $\log A_{iso}$ values calculated from these parameters for seven temperature plots, which compose the series, are presented in Table 2. The regression between the experimental $\log k$ and the $\log k'$ values calculated by formula (3) at the minimum S is expressed by

$$\log k = (1.000\pm0.006)\lg k' + (0.00\pm0.06) \quad (n = 70,\ s = 0.043,\ r = 0.999).$$

A positive T_{iso} value shows that E_{iso} and $\log A_{iso}$ for the members of the series change with a mutual compensation.[1] This behavior is unusual for reactions proceeding through intermediate complexes. Similar reactions in solutions exhibit,[5] as a rule, an anticompensation change in E_{iso} and $\log A_{iso}$. Perhaps, the unusual behavior is a result of a more complicated mechanism of reactions (1) in the gas phase as compared to the common mechanism. The possibility of the contribution of the parallel S$_N$2 reaction of the direct single-step substitution to the total process has been discussed,[22,25] as well as the possibility of the participation of an inert gas, which is present in the system, in the reaction.[25]

Table 3. Activation parameters of reactions (1) in the gas phase calculated using the isokinetic relationship parameters (T_{iso} = 1505 K, $\log k_{iso}$ = 9.972) and theoretically estimated E_a

Reaction	E_{iso} /kJ mol^{-1}	$\log A_{iso}$	E_a /kJ mol^{-1}	Refs.
$PhCH_2Cl$ + Cl$^-$*	11.88	10.384	1.7	27
$PhCH_2Br$ + Br$^-$*	0.68	9.996	−10.5	27
$PhCH_2Br$ + Cl$^-$	−10.82	9.597	−18.8	27
$NCCH_2Cl$ + Cl$^-$*	−11.59	9.570	−24.7	27
$NCCH_2Br$ + Br$^-$*	−10.68	9.602	−30.5	27
$NCCH_2Br$ + Cl$^-$	−16.48	9.401	−41.0	27
MeCl + Cl$^-$*	23.14	10.775	10.5	27
MeBr + Cl$^-$	−1.64	9.916	−7.5	27
MeBr + Br$^-$*	19.15	10.637	—	27
$NCCH_2Cl$ + CN$^-$	−18.78	9.321	−20.1	27
MeBr + Cl$^-$	−1.35	9.926	−2.09**	28
CD_3Br + Cl$^-$	−1.70	9.913	−2.18**	28
MeI + Cl$^-$	−7.44	9.714	−6.74**	28
CD_3I + Cl$^-$	−7.95	9.696	−6.86**	28
MeI + Br$^-$	−1.93	9.905	−2.22**	28
CD_3I + Br$^-$	−2.77	9.876	−2.34**	28

* Isotope exchange reaction.

** E_a were calculated within the 300—400 K interval.

For reactions (1) in the gas phase, the k values are often determined experimentally at the same temperature, and the activation energy is estimated from theoretical calculations. Therefore, Table 3 contains E_{iso} and $\log A_{iso}$ for several reactions estimated from the obtained IKR by the formulas[5]

$$E_{iso} = (\log k_{iso} - \log k)/[(2.303RT)^{-1} - (2.303RT_{iso})^{-1}],$$

$$\log A_{iso} = \log k_{iso} + E_{iso}/(2.303RT_{iso}).$$

A comparison of E_{iso} with E_a calculated by the Reiss—Ramsberger—Kassel—Marcus (RRKM) method[27] shows that the latter are often much lower than those found using IKR, whereas the results in Ref. 28 agree with the data based on IKR. Perhaps, the RRKM theory is not quite appropriate for some nucleophilic reactions in the gas phase.[22]

Some examples of estimations of E_{iso} and $\log A_{iso}$ for reactions in water have been reported.[5] The fulfillment of IKR for reactions (1) in various solvents, which was found in this work, opens up fresh opportunities for predicting the activation parameters of nucleophilic substitution at the saturated carbon atom involving anions in many polar and proton-donor solvents from the known single value of k, whose determination often confines the study of many researchers.

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