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Relationship of the Selectivity Effect of Aromatic Solvents with Their Electron-Donor Ability and Organic Reactant Structure in Free Radical Chlorination

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Abstract—The effect of several solvents on the selectivity of the free radical chlorination of 1,1-dichloroethane and 1-chloropropane is studied. The selective action of aromatic solvents on free radical chlorination is explained. This explanation implies that the process involves solvated chlorine atoms and their donor–acceptor complexes with aromatic molecules (ArH⟶Cl$^{\bullet}$) as intermediates. Using the findings of this work and previous studies, the ratios of the rate constants for hydrogen-atom abstraction from different positions in chloroethane, 1,1-dichloroethane, 1-chloropropane, and 2-chloropropane by solvated chlorine atoms and ArH⟶Cl$^{\bullet}$ complexes are determined. The differences in the activation energies of the competitive hydrogen-atom abstractions from different positions in substrates by the ArH⟶Cl$^{\bullet}$ complexes and solvated chlorine radicals correlate with two HOMO energies of solvent and substrate molecules. The isokinetic relationship is found for all the systems under study (the isokinetic temperature, 523 K).

INTRODUCTION

The effect of aromatic solvents on the selectivity of free radical chlorination is usually explained by the formation of donor–acceptor complexes of chlorine atoms with aromatic molecules (ArH⟶Cl$^{\bullet}$). These complexes exhibit a higher selectivity in hydrogen abstraction as compared to chlorine atoms [1–10]. The relative reactivity of different C–H bonds attacked by the ArH⟶Cl$^{\bullet}$ complexes may be determined by extrapolating the dependences of ratios of the products of competitive chlorination versus ArH concentration to [ArH] = 100%. In this paper, we report our findings concerning the regioselectivity of the chlorination of chloroethane, 1,1-dichloroethane, and 1- and 2-chloropropane. To continue our previous studies [11–15], we investigated how certain aromatic solvents affect the regioselectivity of 1,1-dichloroethane and 1-chloropropane chlorination.

EXPERIMENTAL

The influence of a medium on the chlorination regioselectivity was studied using the ampule method described in [13]. In all the runs, a more than tenfold excess of a substrate with respect to chlorine was used to prevent polychlorination. The chlorination products were analyzed by gas-liquid chromatography on a Tsvet-102 chromatograph equipped with a thermal conductivity detector. The products of 1-chloropropane chlorination were separated on a metallic column (3 m × 3 mm) packed with Chezasorb AW (fraction 0.25–0.36 mm) and tricresyl phosphate (10%). The temperatures of the evaporator, the column, and the detector were 473, 363, and 443 K, respectively. The flow rate of the carrier gas (helium) was 0.7 ml/s. The products of 1,1-dichloroethane chlorination were separated in a metallic column (3 m × 3 mm) packed with Chromaton N-AW-DMCS (fraction 0.16–0.20 mm) and Apiezon L (15%). Products were analyzed at the temperatures of the evaporator, column, and detector (468, 378, and 443 K, respectively) at a carrier gas (helium) flow rate of 0.6 ml/s.

1,1-Dichloroethane and 1,1,1-trichloroethane were commercial regents purified as described in [13]. 1,1,2-Trichloroethane, 1-chloropropane, and 1,1-, 1,2-, and 1,3-dichloropropanes were synthesized and isolated by the procedures described in [16].

To elucidate the relationship between our kinetic parameters and the electron structure of the solvent and reactant molecules, we carried out quantum-chemical calculations of their HOMO energies using a semiempirical quantum-chemical method in the minimal basis set STO-3G. The orbital exponents were taken from [17, 18]. The geometry was optimized by the Fletcher–Reeves method [17, 18]. The molecules with optimized geometries were also calculated using the MNDO quantum-chemical semiempirical method with a standard parametrization [19, 20]. The use of the semiem-

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pirical HOMO energies does not quantitatively affect the activation parameters of the reactions discussed below.

RESULTS AND DISCUSSION

Figure 1 presents typical experimental data that illustrate how aromatic solvents affect the selectivity of the chlorination of the substrates under study and how the product ratio depends on the solvent concentration for 1,1-dichloroethane chlorination in the presence of benzene. Analysis of these and other data on the free radical chlorination of chloroethane, 1,1-dichloroethane, 1-chloropropane, and 2-chloropropane suggests that the ratio of the products of their monochlorination may be approximated by the parabolic equation

$$[A]/[B] = a + b[ArH] + c[ArH]^2, \quad (1)$$

where a is the ratio of the products of monochlorination of a pure substrate at [ArH] = 0 and b and c are the empirical coefficients.

Tables 1 and 2 present our data as parameters of equation (1) corresponding to the experimental conditions. The difference in the reactivities of different substrate positions markedly increases with an increase in the aromatic solvent concentration. A more pronounced change in the product ratio at high temperatures and high solvent concentrations suggests that the energetic factor contributes significantly to a selectivity increase.

According to [8], each competing system may be described by a series of elementary reactions. As hydrogen-abstracting agents, this reaction series includes solvated chlorine atoms and donor–acceptor ArH⟶Cl$^\cdot$ complexes in the following equilibrium with each other

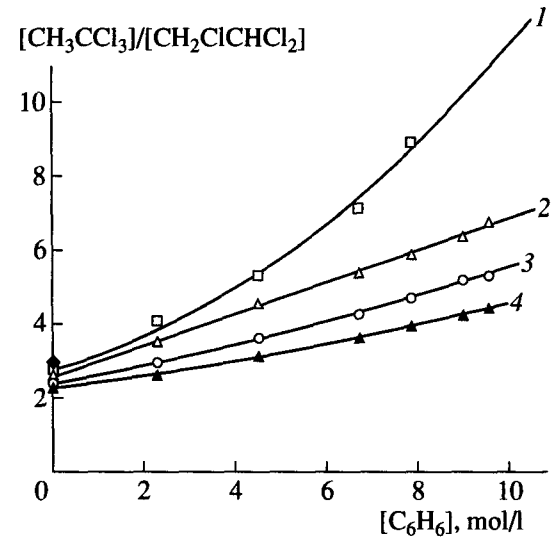

Fig. 1. Ratio of the products of 1,1-dichloroethane monochlorination vs. benzene concentration at temperatures, K: (*1*) 273, (*2*) 293; (*3*) 333, and (*4*) 353 K.

$$ArH + (Cl^\cdot)_{sol} \rightleftharpoons ArH \longrightarrow Cl^\cdot + (Sol). \quad (I)$$

The substrate acts as a solvent incapable of complex formation. For 1,1-dichloroethane chlorination, this system of elementary reactions may be represented as follows:

$$CH_3CHCl_2 \xrightarrow[-HCl\text{–}Sol\ (-HCl\text{–}ArH)]{+(Cl^\cdot)_{sol}\ (+ArH\rightarrow Cl^\cdot)} \begin{cases} \xrightarrow{k_{\alpha 0}\ (k_{\alpha 1})} CH_3\dot{C}Cl_2 \xrightarrow[-Cl^\cdot]{+Cl_2} CH_3CCl_3 \\ \xrightarrow{k_{\beta 0}\ (k_{\beta 1})} \dot{C}H_2CHCl_2 \xrightarrow[-Cl^\cdot]{+Cl_2} CH_2ClCHCl_2. \end{cases}$$

At low conversions and long kinetic chains, the ratio of the chlorination products can be approximated by the formula

$$\frac{[CH_3CCl_3]}{[CH_2ClCHCl_2]} = \frac{\frac{k_{\alpha 0}}{k_{\beta 0}} + \frac{k_{\alpha 1}}{k_{\beta 0}} K \frac{[ArH]}{[CH_3CHCl_2]}}{1 + \frac{k_{\beta 1}}{k_{\beta 0}} K \frac{[ArH]}{[CH_3CHCl_2]}}, \quad (2)$$

where K is the constant of equilibrium (I).

According to formula (2), the ratio of the rate constants for hydrogen-atom abstraction from the α- and β-positions in substrates ($k_{\alpha 0}/k_{\beta 0}$) was determined as the ratio of the products of monochlorination in the absence of aromatic solvents. By applying the Arrhenius equation to these ratios, we obtained the activation parameters (see Tables 3 and 4).

The kinetic analysis of formula (2) shows that, at $\frac{[ArH]}{[CH_3CHCl_2]} \geq 10$, the first terms in both the numerator and the denominator are negligible and the ratio of the monochlorination products may be approximated by the ratio of the rate constants for hydrogen-atom abstraction from the corresponding substrate positions [8]. For example, for 1,1-dichloroethane chlorination in arene, we have

$$\frac{[CH_3CCl_3]}{[CH_2ClCHCl_2]} = \frac{k_{\alpha 1}}{k_{\beta 1}},$$

$$[ArH]/[CH_3CHCl_2] \longrightarrow \infty.$$

Therefore, the ratio of the rate constants for α- and β-H abstraction by the ArH⟶Cl$^\cdot$ complexes ($k_{\alpha 1}/k_{\beta 1}$) was determined by extrapolating the ratios of monochlorination products to a 100% concentration of an aromatic solvent [8]. To do this, we used the least-squares method to determine the parameters b and c (taking into account the experimental parameter $a = k_{\alpha 0}/k_{\beta 0}$) and then calculated the product ratio corresponding to the 100% solvent concentration by equation (1). Pro-

Table 1. Effect of aromatic solvents on the selectivity of the chlorination of chloroethane, 1,1-dichloroethane, and 2-chloropropane

T, K	a	Benzene		Fluorobenzene		Chlorobenzene		Benzotrifluoride		Benzotrichloride		*o*-Dichlorobenzene		1,2,4-Trichlorobenzene*	
		b	c	b	c	b	c	b	c	b	c	b	c	b	c
Chloroethane															
233	2.36	–	–	0.136	0.010	0.212	0.002	0.051	0.005	–	–	0.174	–0.004	–	–
248	2.23	0.139	0.008	0.065	0.011	0.130	0.009	0.023	0.005	0.008	0.033	0.141	–0.004	0.081	–0.004
273	2.11	0.082	0.008	0.042	0.009	0.033	0.010	0.031	0.001	0.002	0.023	0.077	0.002	0.072	–0.004
298	2.02	0.050	0.007	0.015	0.008	0.022	0.008	0.032	0.0002	0.023	0.020	0.037	0.004	0.048	–0.003
1,1-Dichloroethane															
248	2.80	–	–	1.039	0.008	0.407	0.095	0.447	0.014	–	–	0.497	0.040	0.214	0.023
273	2.66	0.347	0.052	0.444	0.024	0.433	0.039	0.250	0.016	0.401	0.024	0.322	0.026	0.119	0.022
293	2.54	0.413	0.002	0.168	0.032	0.435	0.014	0.186	0.011	0.065	0.045	0.170	0.026	0.047	0.025
333	2.34	0.240	0.007	0.105	0.018	0.117	0.025	0.140	0.005	0.012	0.026	0.120	0.014	0.048	0.015
353	2.26	0.164	0.006	–	–	–	–	–	–	0.018	0.022	–	–	–	–
2-Chloropropane															
213	2.68	–	–	–	–	0.544	0.035	–	–	–	–	–	–	–	–
223	2.29	–	–	0.583	0.033	–	–	–	–	–	–	–	–	–	–
243	1.71	–	–	–	–	–	–	0.063	0.013	0.074	0.033	–	–	0.156	–0.003
253	1.64	–	–	0.209	0.020	0.179	0.020	–	–	–	–	0.077	0.010	–	–
263	1.50	0.201	0.028	–	–	–	–	–	–	0.048	0.016	–	–	0.049	0.003
273	1.40	0.183	0.018	–	–	–	–	0.017	0.008	–	–	0.055	0.007	–	–
293	1.20	0.127	0.013	0.118	0.004	0.087	0.006	0.032	0.002	0.004	0.009	0.025	0.006	0.015	0.002
313	1.10	0.115	0.005	0.062	0.005	0.051	0.006	0.009	0.002	0.010	0.008	0.030	2.002	0.010	0.002

* For 2-chloropropane chlorination, benzonitrile was used instead of 1,2,4-trichlorobenzene.

Table 2. Effect of aromatic solvents on the selectivity of 1-chloropropane chlorination

T, K	a	Benzene		Chlorobenzene		Benzotrichloride		*o*-Dichlorobenzene		1,2,4-Trichlorobenzene	
		b	c	b	c	b	c	b	c	b	c
(α/β)*											
213	0.217	–	–	–0.0003	–0.0002	–	–	–	–	–	–
243	0.250	–	–	–0.0002	–0.0002	0.0005	–0.0001	0.0001	0.00001	–	–
263	0.269	–0.0017	–0.0003	–	–	–	–	–	–	–	–
273	0.276	–0.0016	–0.0002	–	–	–0.0018	0.0003	0.0009	–0.00006	0.0034	–0.0004
293	0.296	–0.0023	–0.0002	0.0001	–0.0002	–0.0008	–0.00002	0.0004	–0.00006	0.0031	–0.0003
323	0.331	–0.0029	–0.00005	–0.0017	0.00005	–0.0008	0.0001	–0.00005	0.0001	–0.0004	0.0001
(γ/β)**											
213	0.488	–	–	–0.0252	–0.0002	–	–	–	–	–	–
243	0.573	–	–	–0.0271	0.0003	0.0112	–0.0047	–0.0148	0.0003	–	–
263	0.601	–0.0379	0.001	–	–	–	–	–	–	–	–
273	0.622	–0.0398	0.0012	–	–	0.0062	–0.0036	–0.0035	0.0004	–0.007	–0.00005
293	0.661	–0.0346	0.0007	–0.0201	–0.0002	–0.0056	–0.00080	–0.005	–0.0002	–0.0065	0.00003
323	0.705	–0.0228	–0.00009	–0.0103	–0.0009	–0.0032	–0.0008	–0.0063	–0.00003	–0.0063	0.0001

* The ratio of the products of α- and β-chlorination.

** The ratio of the products of γ- and β-chlorination.

Table 3. Activation parameters of the ratios of the rate constants for hydrogen-atom abstraction from the α and β positions in chloroethane, 1,1-dichloroethane, and 2-chloropropane by solvated chlorine atoms and their ArH⟶Cl˙ complexes ($n = 0$ or 1)

Attacking species	Chloroethane		1,1-Dichloroethane		2-Chloropropane	
	$-\log(A_{\alpha n}/A_{\beta n})$	$-(E_{\alpha n} - E_{\beta n})$, J/mol	$-\log(A_{\alpha n}/A_{\beta n})$	$-(E_{\alpha n} - E_{\beta n})$, J/mol	$-\log(A_{\alpha n}/A_{\beta n})$	$-(E_{\alpha n} - E_{\beta n})$, J/mol
$(Cl^{\cdot})_{Sol}$	−0.072	1330 ± 100	−0.141	1470 ± 50	0.743	4650 ± 200
$C_6H_6 \longrightarrow Cl^{\cdot}$	0.130	3890 ± 100	0.659	9050 ± 200	1.48	11800 ± 600
$C_6H_5F \longrightarrow Cl^{\cdot}$	0.183	3890 ± 250	0.510	7960 ± 20	1.46	10800 ± 250
$C_6H_5Cl \longrightarrow Cl^{\cdot}$	0.220	4050 ± 500	0.515	8100 ± 60	1.26	9500 ± 400
$C_6H_5CF_3 \longrightarrow Cl^{\cdot}$	0.143	2800 ± 300	0.306	5600 ± 250	1.24	8050 ± 300
$C_6H_5CCl_3 \longrightarrow Cl^{\cdot}$	0.189	3700 ± 100	0.417	6400 ± 500	1.39	9150 ± 650
$C_6H_4Cl_2 \longrightarrow Cl^{\cdot}$	0.028	2600 ± 250	0.402	6700 ± 100	1.08	7600 ± 200
$C_6H_3Cl_3 \longrightarrow Cl^{\cdot}$	0.017	2100 ± 300	0.022	3800 ± 50	–	–
$C_6H_5CN \longrightarrow Cl^{\cdot}$	–	–	–	–	0.99	6750 ± 350

Table 4. Activation parameters of the ratios of the rate constants for hydrogen-atom abstraction from the α, β, and γ positions in 1-chloropropane by solvated chlorine atoms and ArH⟶Cl˙ complexes ($n = 0$ or 1)

Attacking species	$-\log(A_{\alpha n}/A_{\beta n})$	$-(E_{\alpha n} - E_{\beta n})$, J/mol	$\log(A_{\gamma n}/A_{\beta n})$	$-(E_{\gamma n} - E_{\beta n})$, J/mol
$(Cl^{\cdot})_{Sol}$	0.208	−1300 ± 200	0.165	−1900 ± 150
$C_6H_6 \longrightarrow Cl^{\cdot}$	0.12	−3400 ± 200	0.586	−5760 ± 300
$C_6H_5Cl \longrightarrow Cl^{\cdot}$	0.06	−2680 ± 200	0.47	−4560 ± 200
$C_6H_5CCl_3 \longrightarrow Cl^{\cdot}$	0.066	−2580 ± 200	0.43	−3750 ± 300
$C_6H_4Cl_2 \longrightarrow Cl^{\cdot}$	0.135	−2180 ± 300	0.34	−3400 ± 200
$C_6H_3Cl_3 \longrightarrow Cl^{\cdot}$	0.21	−1780 ± 200	0.22	−2460 ± 150

cessing the ratios thus obtained using the Arrhenius equation, we determined the activation parameters (Tables 3 and 4).

The differences in the activation energies of competitive hydrogen abstractions by ArH⟶Cl˙ complexes and solvated chlorine radicals ($\Delta E = -(E_\alpha - E_\beta)$) satisfactorily correlate with two HOMO energies of solvents and substrates. This indicates that the electron-donor ability of the solvent (including substrate) molecules dramatically affects the selective action of the medium. Figures 2–4 illustrate the correlations between the ΔE value and the second HOMO energy. The processing of regioselectivity data on the chlorination of chloroethane, 2-cyanopropane, isopropyl acetate, and 1,1,2-trichloroethane [7, 10, 11] in the same coordinates also gives similar correlations (Figs. 2 and 4).

Such correlations are obviously due to a stronger C–H bond stretch in the transition state of hydrogen-atom abstraction by the ArH⟶Cl˙ complexes on passing from less stable to more stable complexes. The reactions involving more stable complexes are more endothermic and, in accordance with the Hammond postulate [21], are characterized by a stronger C–H bond stretch in the transition state. In these cases, the structural possibilities of stabilizing the transition state due to conjugation and hyperconjugation are more pronounced. Because the stability of the attacking ArH⟶Cl˙ charge-transfer complexes depends on the electron-donor properties of the aromatic molecules [22], the relationship between these properties and the relative reactivity is rather reliable.

The slope α of the curves obtained reflects the sensitivity of the selectivity of organic reactant chlorina-

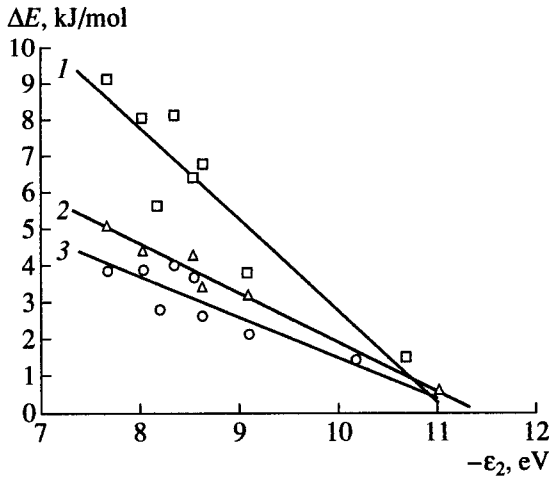

Fig. 2. Difference in the activation energies of hydrogen-atom abstraction from the α and β positions in (*1*) 1,1-dichloroethane, (*2*) 1,1,2-trichloroethane, and (*3*) chloroethane vs. the energy of the second HOMOs of the solvent molecules calculated in the basis set STO-3G. The correlation parameters: (*1*) $\Delta E = 2.50\varepsilon_2 + 27.80$, $r^2 = 0.85$; (*2*) $\Delta E = 1.35\varepsilon_2 + 15.40$, $r^2 = 0.97$; and (*3*) $\Delta E = 1.13\varepsilon_2 + 12.77$, $r^2 = 0.74$.

tion to the electron-donor properties of aromatic solvents. Earlier, we demonstrated the principal role of this parameter, which may be used to predict the selective action of aromatic solvents on free radical chlorination [7]. This sensitivity is obviously due to the relative stability of radicals formed via competitive hydrogen-atom abstraction [7]: the larger the number of structural opportunities for radical stabilization, the more significant the contribution of this stabilization (accompanied by C–H bond stretching) to a decrease in the energy of the transition state. An attempt to relate the sensitivity α to the difference in the energies of substrate HOMOs, the resonance Taft [23] and Swain–Lupton [24] constants, the sum of the contributions of the mesomeric and hyperconjugation effects failed. Apparently, further seeking for the interrelationship between the α value and the structural properties of the substrate molecules should focus on comparing the experimental data with the calculated resonance energies of the resulting radicals and the effects of steric strain removal in the attacking substrate molecules during hydrogen-atom abstraction. The contribution of these effects is confirmed by the data on their regioselectivity in reactions of 2-substituted propanes: the chlorination of isopropyl acetate with a bulkiest substituent is characterized by the maximal α values. The necessity of considering the effect of steric strain removal is supported by the studies on the selectivity of the gas-phase bromination of 1-substituted butanes [25]. In the presence of strong electron-acceptor groups, such as CF_3^-, CF_3COO^-, NC^-, and O_2N^-, in position 1, the C–H bond in this position is much more active as compared to the same bond in the terminal methyl group. Obviously, a higher endothermicity of radical bromination favors C–H bond stretching in the transition state

R···H···Br

and consequently, a more substantial gain in energy upon removing the steric strain. This strain in position 1, occupied by substituents, is much stronger than that in

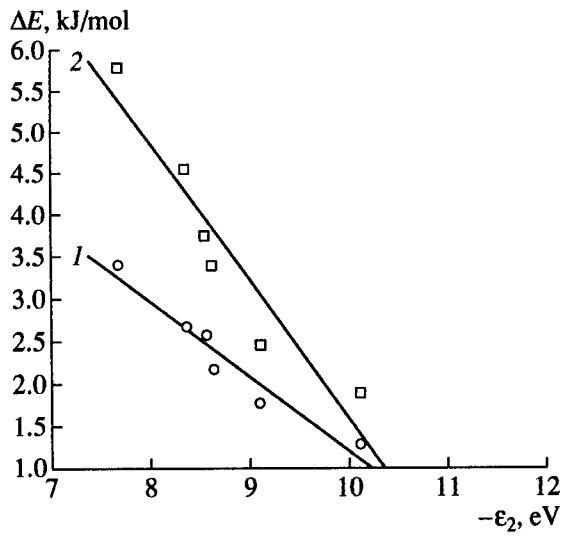

Fig. 3. Difference in the activation energies of hydrogen-atom abstraction from the positions (*1*) α and β and (*2*) γ and β in 1-chloropropane vs. the energy of second HOMOs of the solvent molecules calculated in the basis set STO-3G. The correlation parameters: (*1*) $\Delta E = -(E_\alpha - E_\beta) = 0.88\varepsilon_2 + 9.99$, $r^2 = 0.94$; (2) $\Delta E = -(E_\gamma - E_\beta) = 1.63\varepsilon_2 + 17.88$, $r^2 = 0.89$.

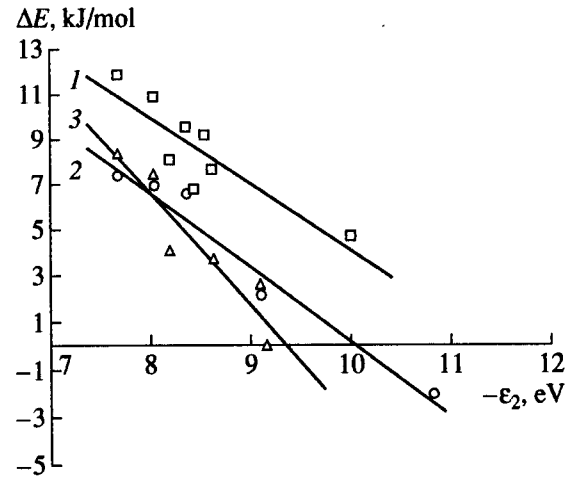

Fig. 4. Difference in the activation energies of hydrogen-atom abstraction from the α and β positions in (*1*) 2-chloropropane, (*2*) 2-cyanopropane, and (*3*) isopropyl acetate vs. the energy of the second HOMOs of the solvent molecules calculated in the basis set STO-3G. The correlation parameters: (*1*) $\Delta E = 2.94\varepsilon_2 + 33.46$, $r^2 = 0.75$; (*2*) $\Delta E = 3.23\varepsilon_2 + 32.46$, $r^2 = 0.95$; and (*3*) $\Delta E = 4.86\varepsilon_2 + 45.52$, $r^2 = 0.87$.

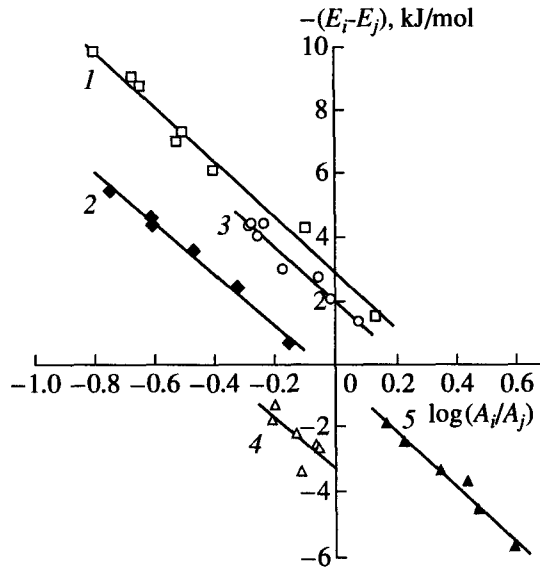

Fig. 5. Isokinetic curves of the activation parameters of competitive hydrogen-atom abstractions from different positions in (*1*) 1,1-dichloroethane, (*2*) 1,1,2-trichloroethane, (*3*) chloroethane, (*4*) 1-chloropropane (α/β), and (*5*) 1-chloropropane (γ/β).

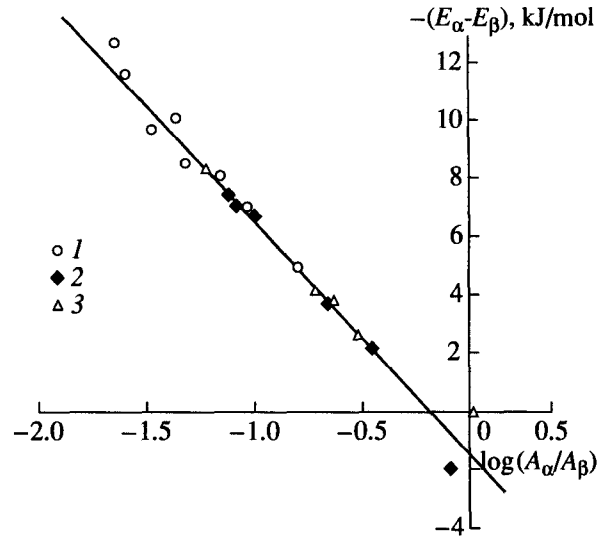

Fig. 6. Isokinetic curve of the activation parameters of competitive hydrogen-atom abstractions from different positions in (*1*) 2-chloropropane, (*2*) cyanopropane, and (*3*) isopropyl acetate.

the terminal methyl group, thus ensuring the energetic preference of 1-bromination.

Analysis of the activation parameters of the k_{i0}/k_{j0} and k_{i1}/k_{j1} ratios ($i = \alpha$ or γ, $j = \beta$) suggests the existence of the compensation effect on changing these parameters, as confirmed by the linear dependence between E_{i1}–E_{j1} (or E_{i0}–E_{j0}) and $\log A_{i1}/A_{j1}$ (or $\log A_{i0}/A_{j0}$) (Figs. 5 and 6). The fact that all data for each system, including those on the chlorination of pure substrates, obey the same isokinetic law indicates the similarity of the transition states of the competitive hydrogen-atom abstractions independently of the type of an attacking species. According to the well-known relation between the activation entropy and the preexponential factor [26], the difference in the activation entropies of the competitive reactions may be represented as follows:

$$\Delta S^{\#} = S_1^{\#} - S_2^{\#} = R\ln\left(\frac{A_1 h}{kT_e}\right) - R\ln\left(\frac{A_2 h}{kT_e}\right),$$

or

$$\Delta S^{\#} = 2.3\log\left(\frac{A_1}{A_2}\right). \qquad (3)$$

The comparison of equation (3) with the isokinetic relation $\Delta E^{\#} = \beta + \gamma\Delta S^{\#}$ [27] shows that the isokinetic temperature may be determined from the slope of the E_{i1}–E_{j1} (or E_{i0}–E_{j0}) vs. $\log A_{i1}/A_{j1}$ (or $\log A_{i0}/A_{j0}$) curve: $\gamma = \tan\delta/(2.3R)$.

The fact that the slopes of the curves in Figs. 4 and 5 are close indicates that the isokinetic temperature is the same for all systems under study. This temperature is 523 K, which is much higher than the upper limit of the temperature range under study. Therefore, the energetic factor plays the main role in changing the selectivity. We believe that the isokinetic relation may be explained by the following physical reasons. More stable ArH⟶Cl˙ complexes exhibit a higher selectivity, which manifests itself in a stronger difference in the activation energies of the competitive reactions. At the same time, a donor–acceptor bond between a chlorine atom and an aromatic molecule in more stable complexes is shorter, and their approach to the C–H bonds in more substituted carbon atoms is hampered by more substantial steric hindrances than the attack of the C–H bonds in less substituted carbon atoms. This explains a change in the preexponential factor ratio and the compensation effect observed when the preexponential factors and activation energy differences are changed. Obviously, the approaching of chlorine atoms, solvated via nonspecific interactions, to the C–H bonds is still less hampered because these interactions are weak. This accounts for the validity of the isokinetic relation for the competitive chlorination of pure substrates.

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