

KINETIC STUDY OF CYCLIZATION
OF 1-ACYL-1'-ALKENOYLFERROCENES. THE EFFECT
OF SUBSTITUTION ON THE DONOR AND ACCEPTOR
OF MICHAEL ADDITION UPON ACTIVATION PARAMETERS
OF THE REACTION

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Two series of disubstituted ferrocenes, 1-acyl-1'-cinnamoylferrocenes and 1-acyl-1'-alkenoylferrocenes, were prepared and kinetics of their cyclization to [5]ferrocenophane-1,5-dione derivatives has been studied. It was found that substitution on the double bond of the acceptor affects the activation parameters of the reaction less than substitution on the donor of Michael addition. Bulky substituents increase markedly ΔH^\ddagger up to 116 kJ mol⁻¹ and ΔS^\ddagger up to +44 K mol⁻¹ K⁻¹.

In the previous work¹ we have studied the kinetics of cyclization of 1-acetyl-1'-(X-cinnamoyl)ferrocenes and investigated especially the effect of polar effects of substituents on the activation of the double bond, *i.e.* the effect of the acceptor of Michael addition. Elečko² reported on the kinetics of cyclization of 1-cinnamoyl-1'-(X-phenylacetyl)ferrocenes and studied thus the effect of polar effects of substituents on the donor of Michael addition. The effect of the size of the cycle formed on the activation parameters of intramolecular Michael addition has been also studied³ as well as the addition of ethyl α -cyanobutyrate to alkenylferrocenes⁴.

The aim of this work was to synthesize suitable 1-acyl-1'-alkenoylferrocenes and to study the kinetics of their cyclization to the corresponding [5]ferrocenophane-1,5-dione derivatives, to obtain the information about the importance of steric factors in the course of this reaction.

EXPERIMENTAL

¹H NMR spectra were measured at 23°C on Tesla BS 487 instrument working at 80 MHz, using solutions of the compounds in CDCl₃ (99.5% of D-isotope) and tetramethylsilane as the internal reference. Chemical shifts were determined with the accuracy of ± 0.01 ppm. UV spectra were recorded and the kinetic study was made with Perkin-Elmer 450 spectrophotometer. Chromatographic experiments were made on SiO₂ columns (Lachema, Brno); the eluent was a benzene-ethyl acetate system (9.5 : 0.5 up to 0:1). Melting points were determined with the use of Koffler apparatus and are not corrected.

1-Acyl-1'-cinnamylferrocenes of the Type A (compounds I—VII)

A solution of 7.5 mmol of the corresponding, freshly distilled acyl chloride in 20 ml of dichloromethane was added under stirring to a solution of 5 mmol of cinnamylferrocene in 40 ml of dry dichloromethane. Then, 10 mmol of anhydrous AlCl_3 were added portionwise into the reaction mixture. After stirring the mixture for 4 h at room temperature, the reaction mixture was poured into ice water. The organic material was extracted with dichloromethane, the dichloromethane solution was washed thoroughly with water and dried over Na_2SO_4 . The solvent was then evaporated and the residue was chromatographed, to give cinnamylferrocene from the first band and another product from the other band. This product was recrystallized from a benzene–light petroleum mixture. Analytical data on the so prepared ferrocene derivatives I—VII are presented in Table I and their ^1H NMR spectra are given in Table II.

1-Acyl-1'-alkenylferrocenes of the Type B (compounds VIII—XIV)

1-Acyl-1'-alkenylferrocenes I, IX—XI and XIV were prepared similarly as the above mentioned compounds, using 0.02 mol of the acylferrocene, 0.03 mol of the appropriate, freshly distilled alkenyl chloride and 0.04 mol of AlCl_3 . A similar procedure was also used to prepare compounds XII and XIII, except that the starting compounds were 4,4-dimethyl-2-pentenylferrocene⁴ and acetyl chloride in the first case and phenylacetyl chloride in the latter. Compound VIII was obtained by the elimination of hydrogen chloride from 1-acetyl-1'-(3-chloropropionyl)-

TABLE I
Analytical data on compounds of type A

No	Compound		Formula mol.mass	Calculated/Found			M.p., °C yield, %
	R ¹	R ²		% C	% H	% Fe	
I	H	H	$\text{C}_{21}\text{H}_{18}\text{FeO}_2$ (358.22)	70.41	5.06	15.59	131—132 54
				70.52	5.12	15.63	
II	H	CH_3	$\text{C}_{22}\text{H}_{21}\text{FeO}_2$ (372.25)	70.98	5.42	15.00	132—134 49
				70.99	5.43	15.11	
III	H	C_2H_5	$\text{C}_{23}\text{H}_{22}\text{FeO}_2$ (386.27)	71.52	5.74	14.46	110—112 22
				71.44	5.87	14.37	
IV	CH_3	CH_3	$\text{C}_{23}\text{H}_{22}\text{FeO}_2$ (386.27)	71.52	5.74	14.46	94—95 63
				71.29	5.84	14.53	
V	H	i- C_3H_7	$\text{C}_{24}\text{H}_{24}\text{FeO}_3$ (400.30)	72.01	6.04	13.95	110—113 29
				72.07	6.17	13.90	
VI	H	C_6H_5	$\text{C}_{27}\text{H}_{22}\text{FeO}_2$ (434.32)	74.60	5.10	12.85	150—152 47
				74.82	4.70	12.95	
VII	H	t- C_4H_9	$\text{C}_{25}\text{H}_{25}\text{FeO}_2$ (414.33)	72.47	6.32	13.48	124 41
				71.95	6.30	13.68	

TABLE II
 ^1H NMR chemical shifts (δ) for compounds of type A

Compound	H	H	H	H	H _a	H _b	Ha _r	CH	CH ₂	CH ₃	J _{ab} (Hz)
I	4-88 t, 1 H	4-55 t, 1 H	4-75 t, 1 H	4-48 t, 1 H	7-08 d, 1 H	7-80 d, 1 H	7,3--7-7 m, 5 H			2-30 s, 3 H	15-5
II	4-85 t, 1 H	4-52 t, 1 H	4-75 t, 1 H	4-55 t, 1 H	7-05 d, 1 H	7-78 d, 1 H	7,3--7-7 m, 5 H		2-65 k, 2 H	1-11 t, 3 H	16-1
III	4-88 t, 1 H	4-55 t, 1 H	4-77 t, 1 H	4-47 t, 1 H	7-08 d, 1 H	7-79 d, 1 H	7,3--7-7 m, 5 H		2-62 t, 2 H	0-94 t, 3 H	16-1
									1-72 kv, 2 H		
IV	4-91 t, 1 H	4-58 t, 1 H	4-81 t, 1 H	4-52 t, 1 H	7-09 d, 1 H	7-80 d, 1 H	7,3--7-7 m, 5 H	3-05 s, 1 H		1-21 d, 6 H	15-6
V	4-88 t, 1 H	4-55 t, 1 H	4-76 t, 1 H	4-47 t, 1 H	7-07 d, 1 H	7-80 d, 1 H	7,3--7-8 m, 5 H	2-23 m, 1 H	2-50 d, 2 H	2-15 d, 6 H	15-7
VI	4-88 t, 1 H	4-57 t, 1 H	4-75 t, 1 H	4-49 t, 1 H	7-09 d, 1 H	7-80 d, 1 H	7,3--7-7 m, 5 H		2-52 s, 2 H	1-02 s, 9 H	15-7
VII	4-81 m, 1 H	4-47 m, 1 H	4-81 m, 1 H	4-47 m, 1 H	7-05 d, 1 H	7-81 d, 1 H	7,0--7-7 m, 10 H		3-95 s, 2 H		15-8

ferrocene, as reported⁵. Analytical data on 1-acyl-1'-alkenoylferrocenes are presented in Table III and their ¹H NMR spectra are given in Table IV.

Kinetic Measurements

Cyclizations of compounds *I–VII* and *VIII–XIV* were carried out at 15–55°C in methanolic solutions ($5 \cdot 10^{-5}$ mol/dm³ initial concentration), using 0.5 mol/dm³ sodium methoxide as the catalyst. The course of the reaction was followed by recording the decrease in the intensity of the long-wave band of the UV spectrum of the starting compound, in which region the product does not exhibit any important absorption (compounds *I–VI*) or this absorption is much lower (compounds *VII–XIII*). Changes in the absorption in dependence on time were calculated from repeated digital records of the spectrum.

Absorbance was measured with the accuracy of ± 0.003 , temperature was maintained with $\pm 0.1^\circ\text{C}$, for prolonged experiments it varied within $\pm 0.3^\circ\text{C}$. The measurements were carried out with the use of automated spectrophotometric system⁶. As the UV light induced the decomposition of starting compounds, the time of irradiation was limited to minimum by using auto-

TABLE III
Analytical data on compounds of type B

	Compound				Formula (mol.mass)	Calculated/Found			M.p., °C yield, %
	R ¹	R ²	R ³	R ⁴		% C	% H	% Fe	
<i>VIII</i>	H	H	H	H	C ₁₅ H ₁₄ FeO ₂ (283.12)	63.86 63.72	5.00 5.07	19.97 20.02	60–61 52
<i>IX</i>	CH ₃	H	H	H	C ₁₆ H ₁₆ FeO ₂ (96.15)	64.89 64.37	5.45 5.46	18.88 19.01	80–82 12
<i>X^a</i>	H	CH ₃	H	H	C ₁₆ H ₁₆ FeO ₂ (296.15)	64.89 65.13	5.45 5.60	18.88 18.97	108–109 47
<i>XI</i>	H	CH ₃	CH ₃	H	C ₁₇ H ₁₈ FeO ₂ (310.18)	65.83 65.62	5.85 5.93	18.00 18.10	57–58 58
<i>XII</i>	H	H	<i>t</i> -C ₄ H ₉	H	C ₁₉ H ₂₂ FeO ₂ (338.23)	67.47 67.52	6.55 6.38	16.51 16.71	80–82 79
<i>XIII</i>	H	H	<i>t</i> -C ₄ H ₉	C ₆ H ₅	C ₂₅ H ₂₆ FeO ₂ (414.44)	72.47 72.48	6.32 6.42	13.48 13.35	128–129 41
<i>XIV</i>	H	CH ₃	CH ₃	C ₆ H ₅	C ₂₃ H ₂₂ FeO ₂ (386.27)	71.52 71.38	6.74 5.81	14.46 14.26	47

^a In the acylation of acetylferrocene by crotonyl chloride, also the cyclization product, 3-methyl-[5]ferrocenophane-1,5-dione has been isolated; m.p. 255–256°C; for C₁₆H₁₆FeO₂ (296.2) calculated: 64.89% C, 5.44% H; found: 64.86% C, 5.43% H.

matically controlled insertion of an partition between the beam and the cell containing the measured sample.

First order rate constants were calculated by Gugenheim method⁷, the reaction order being verified by differential method. Calculations were made at the selected wave length with the use of the whole set of experimental data for the time interval which corresponded to 15–90% conversions, in dependence on the reactivity of the starting compound. The correctness of the calculations was checked also by omitting some (up to 20%) of boundary data from calculations. The results of kinetic experiments are summarized in Tables V and VI.

RESULTS AND DISCUSSION

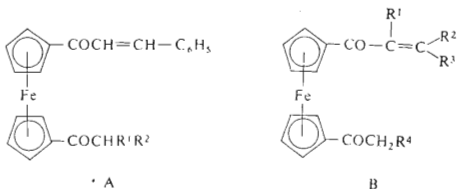
Starting 1,1'-diacetylferrocenes of types A and B were prepared by usual procedures, as described in Experimental part. No attempt has been made to optimize yields. However, the acylation with alkenoyl chloride should be made with freshly prepared and thoroughly distilled acyl chloride, since otherwise only low yields are obtained and the products are strongly impurified. In all the cases, and especially in the acylation with methacroyl chloride, it turned out to be advantageous to follow the reaction course by TLC. This made it possible to stop the reaction before impurities were formed in greater amounts. Furthermore, dichloromethane extracts of reaction mixtures had to be washed thoroughly with water and separated chromatographically immediately after solvent removal by evaporation, since in some cases (compounds IX, X) on longer standing, the crude reaction mixtures undergo a spontaneous

TABLE IV

¹H NMR chemical shifts (δ) for compounds of type B

Compound	H	H	H	H	H _a
VIII	4.83 t, 1 H	4.56 t, 1 H	4.74 t, 1 H	4.50 m, 1 H	6.83 dd, 1 H
IX	4.84 t, 1 H	4.50 m, 1 H	4.74 t, 1 H	4.50 m, 1H	
X	4.81 t, 1 H	4.51 m, 1 H	4.74 t, 1 H	4.51 m, 1 H	6.47 dk, 1 H
XI	4.75 m, 1 H	4.46 m, 1 H	4.75 m, 1 H	4.46 m, 1H	6.30 m, 1 H
XII	4.79 t, 1 H	4.50 t, 1 H	4.70 t, 1 H	4.44 t, 1 H	6.31, d, 1 H
XIII ^a	4.78 t, 1 H	4.46 t, 1 H	4.73 t, 1 H	4.40 t, 1 H	6.32 d, 1 H
XIV	4.75 t, 1 H	4.44 t, 1 H	4.68 t, 1 H	4.32 t, 1 H	6.26 m, 1 H

cyclization to [5]ferrocenophane-1,5-dione derivatives. In most cases the cyclization products were not isolated, since some are already known, *e.g.* those formed by cyclization of the compounds listed in Table I such as *I* (ref.⁸), *II-IV* (ref.⁹) or those formed by cyclization of the compounds listed in Table II, *e.g.* compound *VIII* (refs^{5,10,11}); the product formed from substance *IX* is described in Experimental part. The samples of known cyclization products were used to choose the suitable wave length for kinetic measurements. Attempted cyclization of substance *VII* has not been successful.

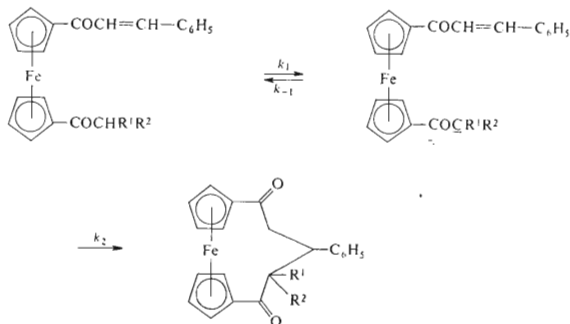


Data presented in Tables V and IV show that ΔH^\ddagger and ΔS^\ddagger values are sometimes laden with large error; this is probably due to the fact that experiments had to be carried out in a narrow temperature range given by the boiling of the solvent used

TABLE IV
(Continued)

H_b	H_x	$COCH_3$	$COCH_2PH$	J (Hz)
6.47 dd, 1 H		2.34 s, 3 H		$J_{ab} = 17, J_{ab'} = 9.8$
5.69 dd, 1 H				$J_{bb'} = 2.6$
5.75 m, 1 H	2.03 m, 3 H	2.35 s, 3 H		$J_{bb'} = J_{bx} 1$
5.66 m, 1 H				
7.09 m, 1 H	1.95 dd, 3 H	2.34 s, 3 H		$J_{ab} = 15.2, J_{ax} 1$
	2.23 d, 3 H	2.32 s, 3 H		$J_{bx} = 6.2$
	1.97 d, 3 H			$J_{ax} 1$
7.08 d, 1 H	1.10 s, 9 H	2.28 s, 3 H		$J_{ab} = 15.9$
7.08 d, 1 H	1.14 s, 9 H		3.93 s, 2 H	$J_{ab} = 15.8$
			7.32 m, 5 H	
	2.18 d, 3 H		3.90 s, 2 H	$J_{ax} 1$
	1.92 d, 3 H		7.26 m, 5 H	

and also by rather low reactivity of some compounds (particularly III–V) which led to establishment of the equilibrium at low conversion. Standardization of spectral data and their automated treatment allowed to achieve the accuracy of ± 1 per cent in the rate constant determination. Before entering into discussion of obtained results, it has to be clarified whether the experimental rate constants characterize the cyclization step (k_2) or whether they are affected also by the equilibrium between the methoxide ion and the donor of Michael addition, *i.e.* k_1/k_{-1} (Scheme 1).



SCHEME 1

We assume that the preceding acid–base equilibrium establishes fast and that thus $k_{\text{obs}} = k_2$, irrespective of the observed dependence of k_{obs} on the concentration

TABLE V
Kinetic parameters of cyclization of compounds of type A

Com- pound	λ nm	$\log \epsilon$	λ nm	$\log \epsilon$	$k \cdot 10^4 \text{ (s}^{-1}\text{) at}$				ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹
					35°C	45°C	50°C	55°C		
I	307	4.154	222	4.165	1.071	2.866	4.197	6.363	74.60 \pm 1.97	-86.94 \pm 5.86
II	310	4.475	224	4.487	1.873	5.282	8.657	13.093	79.71 \pm 2.10	-58.74 \pm 4.20
III	308	4.051	222	4.079	1.600	4.803	8.264	13.608	88.20 \pm 2.10	-39.66 \pm 2.30
IV	307	4.148	222	4.159	0.132	0.423	0.925	1.458	103.51 \pm 5.40	-11.05 \pm 1.50
V	310	4.464	223	4.492	0.0158	0.075	0.165	0.267	116.02 \pm 7.20	+13.22 \pm 2.43

TABLE VI
Kinetic parameters of cyclization of compounds of type B

Compound	λ nm	$\log \varepsilon$ nm	λ	$\log \varepsilon$	$k \cdot 10^3 (s^{-1})$ at			ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	
					15°C	20°C	25°C			30°C
VIII	277	3-662	241	3-945	102-360	127-520	168-390	199-220	33-05 ± 3-77	-157-65 ± 36-43
IX	265	3-903	221	4-093	14-171	19-839	29-147	39-745	50-17 ± 1-17	-114-77 ± 11-30
X	265	3-645	221	3-992	2-015	3-321	4-939	6-800	59-16 ± 3-77	-108-46 ± 2-08
XI	267	3-984	222	4-079	0-832	1-355	2-242	3-601	72-01 ± 2-43	-65-23 ± 5-44
XII	266	4-283	236	4-390	0-139	0-257	0-475	0-838	86-82 ± 1-63	-25-77 ± 0-38
XIII	268	4-328	222	4-515	0-097	0-097	0-222	0-462	110-75 ± 2-34	+45-19 ± 2-50
XIV	277	4-004	241	4-277	0-579	0-977	1-661	2-655	73-97 ± 0-80	-58-66 ± 1-72
VI	305	4-468	223	4-497	281-700	407-860	619-740	810-660	52-09 ± 2-51	-102-17 ± 2-92

of methoxide ions¹. This presumption is justified by the finding that immediately after addition of the alcoholate to the reaction mixture, the absorption in the long-wave maximum region increases, most likely due to formation of the enolate ion. The increase in the absorption which was not time-dependent, was observed also after addition of sodium methoxide to acetylferrocene or *t*-butylacetylferrocene solutions. Another support for this assumption follows also from the fact that all the derivatives but compound *VI* possess only alkyl groups on the donor. According to Charton¹², these groups have essentially identical inductive effect. (Differences in Taft σ^* constants are due to steric factors). Therefore, the acidity of donor hydrogens as well as the thermodynamic stability of the carbanions formed would not change substantially, except for compound *VI*.

In the light of the above facts, the study of activation parameters of the cyclization of 1-acyl-1'-cinnamoylferrocenes (Table V) can provide information about the influence of steric factors on the donor of Michael addition on its course. It is worthy of note that the more detailed study of this factor has not yet been performed for any type of Michael addition¹³. From data presented in Table V it becomes evident that the cyclizations under study are characterized by high ΔH^\ddagger which increases strongly with the size of substituents from 74 to 116 kJ mol⁻¹. The effect of steric factors or of the size of the substituent on the donor of the addition is even more pronounced in the case of ΔS^\ddagger which changes from negative value -87 J mol⁻¹ K⁻¹ to positive value +13 J mol⁻¹ K⁻¹. The derivative substituted by *t*-butyl group on the donor of the addition (compound *VII*) could not be cyclized. Such a change in the activation entropy is surprising, since we do not deal here with solvolytic reactions. Although a similar effect of steric factors (increase in ΔS^\ddagger) was observed for bimolecular nucleophilic substitution on (h⁶-arene)-(h⁵-cyclopentadienyl)iron cations¹⁴ and for the acid catalysed isomerisation of *cis*-1,2-diarylacrylonitriles¹⁵, the explanation of this phenomenon did not receive proper attention.

The sequence of reactivity and activation parameters of the cyclization found in this work can be explained by assuming that the difference between the arrangement of the initial and transition state decreases with increasing bulk of groups on the donor of Michael addition. In other words, the initial state is assumed to be well arranged. This can be accounted for by hypothesis that in studied derivatives (and in protic solvent used) rotation around the axis passing through the centre of cyclopentadiene rings (Cp) and iron atom is hindered and antiperiplanar arrangement of studied compounds is preferred also in solution. It seems likely that the important role is played by solvation of enolate ions and carbonyl groups by methanol molecules, since the study of rotation around C₅ axis in 1,1'-dihalogenoferrocenes in *n*-decane proved¹⁶ that even for 1,1'-diiodoferrocene, the rotation barrier is very low and equals to approx. 6 kJ mol⁻¹. The introduction of bulkier substituents into ferrocene molecule can increase this barrier up to 11 kJ mol⁻¹, as exemplified on esters of 1,1'-dicarboxylic acid with 4-hydroxy-2,2,6,6-tetramethylpiperidine

N-oxide¹⁷. The unambiguous explanation of the observed dependence of ΔS^\ddagger on steric effect of substituents can provide, however, the planned study of analogous factors in the intramolecular addition.

The possibility that the cyclization of 1-cinnamoyl-1'-(3,3-dimethyl)butyrylferrocene would be prevented by the fact that this molecule is not able to form carbanion can be disregarded in the light of the proved H/D isotopic exchange. As found by ¹H NMR spectroscopy, the half time of H/D exchange of hydrogens of the methylene group in compound VII equals to 70 min. It is worthy of note that the half time of H/D exchange of acidic hydrogens in acetylferrocene is 5 min and in 3,3-dimethylbutyrylferrocene it is 2 h under the same conditions. It is necessary to keep in mind that in kinetic study of cyclization we have worked at substantially higher sodium methoxide concentrations or at lower FcCOR/CH₃ONa ratio than in the case of the H/D exchange experiments. From the above mentioned facts it follows that the differences in the kinetic acidity of hydrogens of the —CO—CH₂R groups cannot affect significantly the rate constant of cyclization (k_2), since these cyclizations proceeded at a slow rate (reaction time up to 70 h). This hypothesis is valid only under condition that the equilibrium concentration of the carbanion is not function of steric demands of the group R.

It can be hardly expected that the cyclization of compound VII was not observed because of the low conversion. Synthetic experiments of the cyclization in ethanol or in an ethanol–water mixture, *i.e.* in the medium in which the cyclization products are insoluble (which shifts the equilibrium to the side of products) have been also unsuccessful.

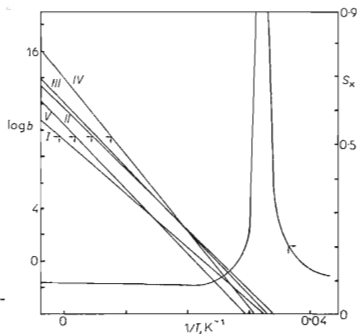


FIG. 1

Isokinetic relation for cyclization of 1-acyl-1'-cinnamoylferrocenes of type A

At first sight it is striking that the cyclizations of 1-cinnamoyl-1'-phenylacetylferrocene leading to 2,3-disubstituted [5]ferrocenophane-1,5-diones took place easily², and, particularly, that also the cyclization of 1-(4,4-dimethyl-2-pentenoyl)-1'-phenylacetylferrocene (*XIII*) could be realized. As from both compound *VII* and *XIII*, isomeric 2,3-disubstituted [5]-ferrocenophane-1,5-diones would be formed which have only exchanged substituents in positions 2 and 3, the unsuccessful cyclization of compound *VII* cannot be explained by steric strain in the product or by steric interactions in the transition state. This different reactivity of both compounds can be attributed to the different structure of intermediates, carbanions. In the carbanion formed from phenylacetyl group one can expect the planar structure with delocalization of charge also on the benzene ring, which would lead to lesser solvation. This would result in the lower barrier to rotation around the Cp-Fe-Cp axis. It seems likely that the reaction is also affected by the fact that in compound *XIII* the bulky t-butyl group is bonded rigidly to the sp^2 carbon and exerts thus smaller steric hindrance to rotation.

Data presented in Table VI document the effect of substitution of hydrogens bonded to the double bond of the acceptor on the course of intramolecular Michael addition. At first sight it becomes clear that each substitution makes the reaction less easier, which reflects in the increase in ΔH^\ddagger and ΔS^\ddagger . This change is impressive from ΔH^\ddagger 33.05 kJ mol⁻¹ and ΔS^\ddagger -157.6 J mol⁻¹ K⁻¹ for COCH=CH₂ derivative to ΔH^\ddagger 86.9 kJ mol⁻¹ and ΔS^\ddagger -25.77 J mol⁻¹ K⁻¹ for -COCH=CH-C(CH₃)₃ derivative. The activation entropy $\Delta S^\ddagger = -157.0$ J mol⁻³ for the cyclization of compound *VIII* is even higher than in the diene synthesis¹⁸, which indicates the great change in the arrangement between the initial and transition state. The substitution of hydrogen for t-butyl group (compound *XII*) indicates that in this case also the initial state must be very arranged. It is of interest that the effect of substitution on the α carbon manifests itself more distinctly than the effect of substitution on the β carbon, in agreement with reported qualitative data^{19,20}.

The two, last but one, data from Table VI document that while the substitution of the methyl group of 1-acetyl-1'-(3-methylbutenoyl)ferrocene by phenyl does not affect significantly the course of the reaction, such a substitution in 1-acetyl-1'-(4,4-dimethyl-2-pentenoyl)ferrocene has strong influence. It is probable that this is caused by accumulation of bulky substituents in this ferrocene derivative (compound *XIII*).

The series of five compounds of type A was tested on the validity of isokinetic relation. On the basis of standard deviations $s_0 = 0.073$, $s_{00} = 0.081$; $s = 0.086$; $s_R = 0.843$ and $s_T = 0.357$ we assume that we deal here with the isoenthalpic reaction series, $T = 417$ K (Fig. 1). As it is seen from Fig. 1, the boundary substituents (substances *I* and *IV*) show relatively large deviation, which reflects also in large errors in the correlation of $\log k_{35}$ with E'_s reported in ref.²¹. We found the following parameters of the correlation: $\delta = 2.24$, $r = 0.92$, $q = 3.63$, $s_r = 0.3$ and $s_\sigma = 0.52$

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