KINETIC STUDY OF CYCLISATION OF SOME FERROCENE DERIVATIVES TO [m]FERROCENOPHANES

[a]M.Livař, [b]M.Sališová and [b]Š.Toma

[a]*Institute of Chemistry, Comenius University and*
[b]*Department of Organic Chemistry and Biochemistry,*
Comenius University, 80 100 Bratislava

A kinetic study was made of intramolecular Michael addition of some ferrocene derivatives to [m]-ferrocenophanes. The effects of size and structure of the bridge on activation parameters are discussed. Experimental data indicate that [4] and [5]ferrocenophane derivatives are most readily formed.

The intramolecular Michael addition can be used with advantage for preparing bridged ferrocene derivatives, particularly derivatives of [5]ferrocenophanes[1,2]. The reaction of this type has been used to synthesise both [4], [3], and [7]ferroceno-phanes[3,4] and bridged derivatives in which one *m*- or *p*-phenylene group, or two *p*-phenylene groups are the constituent of the bridge[5]. Little attention has been paid to the kinetics of the reaction[6]. In this work the kinetic study of the intramolecular Michael addition was made with the aim of ascertaining the relation between the activation energy and entropy and the size of the bridge.

EXPERIMENTAL

Compounds used. Preparations of compound[4] *I* (Table I), the product of its cyclisation[4], sub-stances *V*, *VI*, and *VII* (ref.[5]) and the products of their cyclisation[5] were already reported as indicated. The substance *IV* and the product of its cyclisation[11] as well as compound[12] *II* and the product of its cyclisation[12] were also reported.

1-*Acetyl*-1-(4-*chlorocinnamoyl)ferrocene* (III) was prepared similarly as substance *II*, 79% yield, red crystals of m.p. 167°C (benzene). For $C_{21}H_{17}ClFeO_2$ (392·7) calculated: 14·22% Fe, 9·08% Cl; found: 14·40% Fe, 9·31% Cl.

3-(4-*Chlorophenyl)[5]ferrocenophan*-1,5-*dione* was obtained by cyclisation of *III* induced by sodium hydroxide in ethanol. For the procedure see ref.[4]; 92% yield, m.p. 305°C (dec.). For $C_{21}H_{17}ClFeO_2$ (392·7) calculated: 14·22% Fe, 9·08% Cl; found: 14·67% Fe, 9·28% Cl.

Kinetic study of the cyclisation of compounds *I* — *VII* (Table I) was made at 20 — 60°C in metha-nolic solutions (c 6 . 10^{-5}M), using sodium methoxide as a catalyst (c 0·5M). The decrease in concentration of the starting compound was followed spectrophotometrically, by measuring the absorption of the band at 310 nm. At this wavelength the reaction product did not show any

significant absorption. Absorbancy changes in dependence on time were evaluated from repeated digital records of the spectra. The spectra were recorded at five wavelengths chosen from the 290 to 330 nm region. The absorbancy was measured with an accuracy of ± 0.003, the temperature was maintained within $0.1°C$, at lengthy experiments (to 30 h) it changed within $0.3°C$. The measurements were performed with the use of the automatic spectrophotometric system described earlier[7]. Because UV light induced changes in the reaction mixture, the time period for which the samples were exposed to UV light between individual records was kept at minimum by an automatically controlled diaphragm which was placed to optical path in front of the cell containing sample.

First-order rate constants were calculated according to Guggenheim[8]. The calculation was made at each wavelength for the whole set of experimental data obtained for the time interval followed (which corresponded to 15—90% conversion, in dependence on the reactivity of the compound investigated). Then, the calculation was repeated with the sets of data the number of which was gradually reduced to 1/3 of the number of the initial points. In Table I are included the results for which the values of rate constants for individual wavelengths and different sets of data differed from one another by less than 3%.

RESULTS AND DISCUSSION

The acquirement of sufficiently accurate data was made difficult by following factors: side and consecutive reactions observed with some derivatives studied; the narrow temperature interval, the upper limit of which was given by boiling point of the solvent and the lower limit by reasonable reaction time (30—40 h). In some cases, also a low conversion, *i.e.* a small change in absorbancy, was a serious problem. By standardisation of spectral data and by their automatic treatment, the values of

TABLE I

Activation Parameters of Cyclisation of 1,1′-Disubstituted Ferrocenes to [*m*]Ferrocenophanes at 314 K

Starting compound	R^1	R^2	E kcal mol^{-1}	$\Delta S^{\ddagger}$ cal mol^{-1} grad^{-1}
Ia	CH_3CO	$4\text{-}ClC_6H_4\text{—}CH\text{=}C\text{—}$ $\mid$ CN	17.04 ± 0.54	-17.74 ± 6.16
IIa	CH_3CO	$C_6H_5\text{—}CH\text{=}CH\text{—}CO\text{—}$	18.41 ± 0.36	-19.43 ± 2.6
IIIa	CH_3CO	$4\text{-}ClC_6H_4\text{—}CH\text{=}CH\text{—}CO\text{—}$	18.76 ± 0.50	-17.95 ± 5.3
IVa	CH_3CO	$C_6H_5\text{—}C\text{≡}C\text{—}CO\text{—}$	18.97 ± 0.49	-16.98 ± 3.4
Va	$3\text{-}CH_3COC_6H_4$	$C_6H_5\text{—}CH\text{=}CH\text{—}CO\text{—}$	16.37 ± 1.19	-28.79 ± 8.5
VIa	$3\text{-}CH_3COC_6H_4$	$4\text{-}ClC_6H_4\text{—}CH\text{=}CH\text{—}CO\text{—}$	18.72 ± 0.80	-20.17 ± 6.7
VIIa	$4\text{-}CH_3COC_6H_4$	$4\text{-}ClC_6H_4\text{—}CH\text{=}CH\text{—}CO\text{—}$	20.59 ± 2.40	-19.89 ± 12.7

rate constants were obtained with an average accuracy of $\pm 1\%$. In each experiment, the validity of the rate equation was tested by following the dependence of rate constant on the interval of selected experimental data (Fig. 1). The independence of the rate constant on wavelength (within 3%) indicated that the reaction has a simple course. In spite of this fact the estimated relative standard deviation for the frequency factor in the Arrhenius equation equaled to 25%, which unfavourably influenced the values of standard deviations of $\Delta S^{\pm}$ (Table I).

As can be seen from Table I, the activation energy $E^{\pm}$ and the entropy $\Delta S^{\pm}$ of studied reactions has a value of approx. 18 kcal mol^{-1} and -20 cal grad^{-1} mol^{-1}, respectively. From comparison of these results with the data reported[9] for the addition of ethyl 2-cyanobutyrate to chalcones ($\Delta H^{\pm} \sim 10$ kcalmol^{-1}, $\Delta S^{\pm} \sim$ ~ -35 cal grad^{-1} mol^{-1}) it becomes clear that the intramolecular Michael additions studied in this work require twofold higher activation energy, while the change of entropy between the initial state and the activated complex is approx. half of that for the cited reaction. This may be related to the fact that the cyclisations under study are monomolecular, *i.e.* formation of the activated complex is accompanied by change of the degree of freedom of only one molecule, while the addition of ethyl 2-cyano-butyrate to chalcones is bimolecular, *i.e.* the degrees of freedom of both reacting components are changed. It can be said, however, that a considerable change in freedom or in the arrangement of the system occurs on going from the initial state
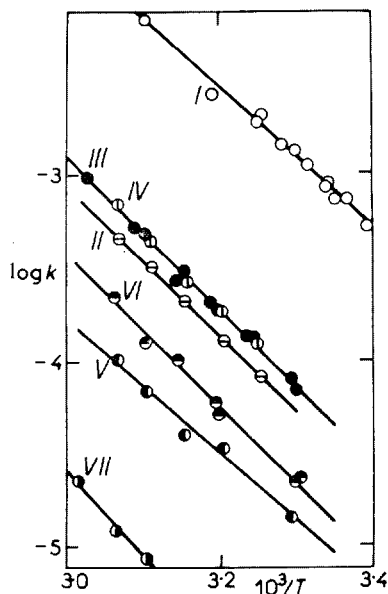

FIG. 1

Temperature Dependence of Rate Constants (log k, s^{-1}) of Cyclisation of Ferrocene Derivatives to [n]Ferrocenophanes

The compounds are denoted as in Table I, ○ *I*, ⊖ *II*, ● *III*, ◌ *IV*, ◑ *V*, ◓ *VI*, ◐ *VII*.

to the activated complex, since the $-\Delta S^{\neq}$ found are high and comparable even with the activation entropies of some diene syntheses[10] (-25 cal grad^{-1} mol^{-1}). The fact that in the transition state the rotation of cyclopentadienyl rings of ferrocene around the axis passing through their center and Fe atom must be retarded might contribute to the comparatively high activation entropy. A more detailed comparison of the activation entropies (Table I) does not seem to be justified, because of high values of standard deviations of $\Delta S^{\neq}$. Repeated measurements showed, however, that the $\Delta S^{\neq}$ values calculated from different sets of experimental points differ from one another only little, although their standard deviations are high. This enables us to make some conclusions. From comparison of the activation entropies for compounds *II* and *IV* it follows that the cyclisation which leads to the derivative of [5] ferrocenophane containing the double bond is characterised by lower $-\Delta S^{\neq}$. This may be due to the fact that the cyclisation of 1-acetyl-1'-cinnamoylferrocene (*II*) proceeds through the activated complex of higher orderliness, since the reagent ($-COCH_2^{(-)}$) can approach the double bond only from below the double bond plane (the bond cannot be formed if attack by the reagent occurs from the side of the H or C_6H_5 group attached to the β-carbon of the double bond). This is not the case with 1-acetyl-1'-(3-phenylpropiolyl)ferrocene (*IV*) which is a linear system.
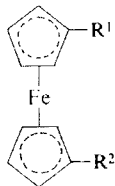
Ia — VIIa   *Ib — VIIb*

R^1 and R^2
see Table I
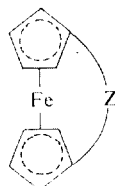
Ib, Z $=$ $-CO-CH_2-CH(C_6H_4Cl-(p))-CH(CN)-$

IIb, Z $=$ $-CO-CH_2-CH(C_6H_5)-CH_2-CO-$

IIIb, Z $=$ $-CO-CH_2-CH(C_6H_4Cl-(p))-CH_2-CO-$

IVb, Z $=$ $-CO-CH=C(C_6H_5)-CH_2-CO-$

Vb, Z $=$ $-CO-CH_2-CH(C_6H_5)-CH_2-CO-m-C_6H_4-$

VIb, Z $=$ $-CO-CH_2-CH(C_6H_4Cl-(p))-C_6H_4-CO-m-$
$-C_6H_4-$

VIIb, Z $=$ $-p-C_6H_4-CO-CH_2-HC(C_6H_4Cl-(p))-CH_2-$
$-CO-p-C_6H_4-$

The activation entropy of cyclisation of 1-(3-acetylphenyl)-1'-cinnamoylferrocene (*V*) is high. This is probably due to the fact that the cycle formed is very rigid and the transition state must be highly arranged. Further, the study of Dreiding models revealed that due to the interaction of hydrogen atoms of the benzene ring with hydrogens of the bridging $-CH_2-$ groups the reaction product, and likely, at least

to a certain extent, also the transition state, are considerably sterically strained. The activation energy as well as activation entropy for compound *V* and its analogue *VI* differ markedly from one another, which is not observed with compounds *II* and *III*. This raises the question whether the rate constants obtained by us characterise the „pure" cyclisation or whether they are influenced by retro-Claisen–Schmidt reaction by which the concentration, and thus also the absorbance, of the starting compound is decreased. It was observed that in some cases the substitution by halogen facilitates such a reaction[4]. Unlike compound *V*, the transition state of the reaction of 1-(4--acetylphenyl)-1'-4-(4-chlorocinnamoyl)phenylferrocene *(VII)* is symmetrical and there is no reason which would lead to high values of activation entropy. The compound can be thus compared with the substance *II*. Comparatively great error in the determination of the activation energy is caused by the fact that the reaction stops at low conversion. For this reason we were able to measure only rate constants for very narrow temperature interval.

Apart from above-mentioned compounds, 1-phenyl-3-(1'-acetylferrocenyl)-2--propene-1-one, which would yield corresponding [3]ferrocenophane, and 5-1-(4--chlorocinnamoyl)ferrocenyl-2-butanone, which would afford corresponding [7]ferrocenophane, were subjected to cyclisation. Because of great number of competitive and consecutive reactions[4], the course of the reactions could not be followed kinetically.

REFERENCES

1. Mashburn T. A. jr, Cais C. G., Hauser C. R.: J. Org. Chem. *25*, 1982 (1960).
2. Furdík M., Toma Š., Suchý J., Elečko P.: Chem. zvesti *15*, 45 (1961).
3. Horspool W. M., Sutherland R. G.: Chem. Commun. *1967*, 240.
4. Toma Š., Sališová M.: J. Organometal. Chem. *57*, 191 (1973).
5. Toma Š., Sališová M.: J. Organometal. Chem. *57*, 199 (1973).
6. Elečko P.: Chem. zvesti *23*, 212 (1969).
7. Livař M., Hrnčiar P., Macháčková M.: This Journal *37*, 1150 (1972).
8. Guggenheim E. A.: Phil. Mag. *2*, 538 (1926).
9. Toma Š.: This Journal *34*, 2771 (1969).
10. Gould E. S.: *Mechanismus und Struktur in der Organischen Chemie*, p. 218. Verlag Chemie, Weinheim 1964.
11. Elečko P., Solčaniová E., Toma Š.: Chem. zvesti, in press.
12. Toma Š.: This Journal *34*, 2235 (1969).

Translated by J. Hetflejš.