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Kinetics of the synthesis of the *S*-(1-ferrocenylethyl)thioglycolic acid

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Abstract

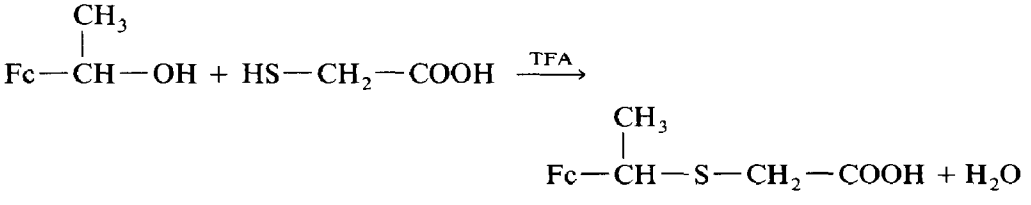
A systematic study of the reactions of a number of α-hydroxylated ferrocene derivatives with thioglycolic acid confirms that the reaction is extremely fast, viz., 15–20 min [1], as compared with earlier procedures (12 h) [2,3]. The important kinetic parameters of the reaction of 1-ferrocenylethanol with the thioglycolic acid in the presence of trifluoroacetic acid have been determined.

Introduction

On the basis of the high reactivity and selectivity of the mono- and dihydroxylated derivatives of ferrocene in the reaction with the thioglycolic acid in the presence of trifluoroacetic acid (TFA), the present paper outlines various aspects on the kinetics and the mechanism of the reaction.

Results and discussion

The model substrate 1-ferrocenylethanol was used in the study, as it is known to show complete retention of configuration in the reaction [2]:



$$Fc-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + HS-CH_2-COOH \xrightarrow{TFA} Fc-\underset{\displaystyle CH_3}{\underset{|}{CH}}-S-CH_2-COOH + H_2O$$

($Fc = C_5H_5FeC_5H_4$)

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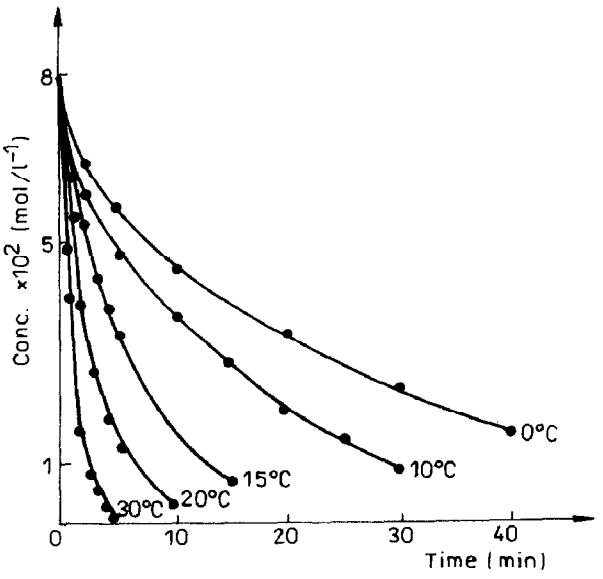

Fig. 1. Kinetic curve of 1-ferrocenylethanol.

Complete retention of configuration is frequently encountered in ferrocene derivatives that have had the readily transferable groups at the C_{sp^3} substituted with a ferrocenyl unit. The retention of configuration can be explained if it is assumed that the reaction develops by a S_N2 mechanism (two successive inversions of

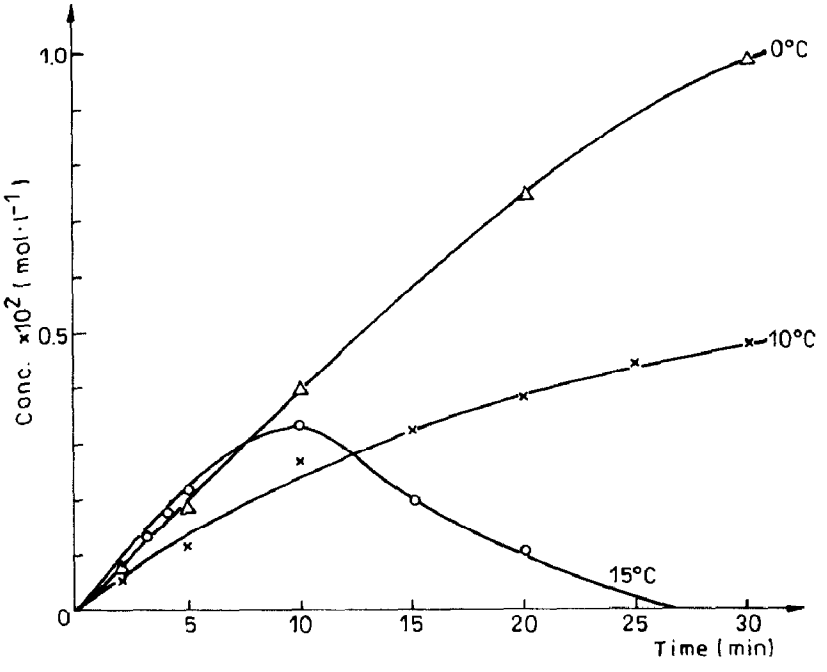

Fig. 2. Kinetic curve of vinylferrocene.

Table 1

Kinetic parameters of the reaction of 1-ferrocenylethanol with thioglycolic acid

No.	T(°C)	n [a]	k (min^{-1}) [b]	$\tau_{1/2}$ (min) [c]
1	0	1.065	0.04226	15.0
2	10	1.240	0.07853	8.0
3	15	1.177	0.11916	3.5
4	20	1.175	0.26968	1.8
5	30	1.122	0.78852	0.9

[a] n = reaction order. [b] k = rate constant. [c] $\tau_{1/2}$ = half-time.

configurations) or by a S_N1 mechanism, in the latter case the α-ferrocenyl radical enhances nucleophilic attack on the reaction center.

Kinetic studies have shown that, in the concentration range used, the reaction is first order, which implies the appearance in the system of a ferrocenylcarbenium ion, whose high stability is unanimously recognized. From extended Hückel calculations was generated a minimum energy structure, in which the rings are tilted and the C_{exo} is displaced from the plane of the adjacent ring towards the iron atom [4]. Such a structure requires participation by the metal at the reaction center, which thus explains the stereoselectivity during the nucleophilic attack.

The reactions were monitored by thin layer chromatography and permitted the identification of the vinylferrocene that results from a competitive elimination reaction.

Owing to the complexity of the reaction medium, the concentrations of the products were determined spectrophotometrically, after the reaction had been quenched with triethylamine (TEA) and the components had been separated by quantitative TLC. Figures 1 and 2 plot the kinetic curves of the 1-ferrocenylethanol and vinylferrocene. The kinetic data are listed in Table 1.

The experimental data indicate that the amount of vinylferrocene produced falls with rise in temperature (20.87% at 0 °C, 6.89% at 10 °C, max. 4.12% at 15 °C, and below the limit of detection at 20 and 30 °C). Surprisingly, the vinylferrocene concentration reaches a maximum after 10 min at 15 °C but dwindles to below the detection limit at the end of the reaction; this behaviour can be explained in terms of the enhanced affinity of the α-ferrocenylethyl cation towards water, as the temperature is increased.

The activation energy, determined from the Arrhenius equation is 83.042 kJ/mol, which is consistent with the rapid rate of the reaction.

Experimental

1-Ferrocenylethanol was prepared by the reduction of acetylferrocene and purified by column chromatography.

Thioglycolic acid was used as supplied by Merck. Trifluoroacetic acid (Fluka) was distilled before use. TLC analyses and preparative separations on plates were performed with Silicagel FG 254 supplied by Merck. The plates were activated at 150° for 2 h.

The kinetic study was performed at 5 different temperatures (0, 10, 15, 20 and

30 °C) in CH_2Cl_2 solutions (8×10^{-2} *M*), using TFA as catalyst (0.5×10^{-3} *M*). The reaction was quenched with TEA.

Separation of 1-ferrocenylethanol from vinylferrocene was performed by use of a 10/2 benzene-acetone mixture as eluent ($R_{f\,alcohol} = 0.62$, $R_{f\,alkene} = 0.92$). The spots corresponding to 1-ferrocenylethanol and vinylferrocene were removed quantitatively, extracted with CH_3OH Spectranal (Merck), and readings were taken on a Pye–Unicam spectrophotometer, at $\lambda = 430$ nm.

Concentrations were determined from standard curves plotted under conditions similar to those applied in the isolation of compounds from the reaction medium. The sensitivity of the method was 1 gamma and the reproducibility was 90%. The data obtained are each presented as the mean of three determinations.

The reaction order was determined by use of a graphical derivation program, on a TIM-S type computer. The rate constants were calculated from the linearized integral kinetic equation of the first order, as determined by graphical derivation.

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