

OXIDATION OF (1-HYDROXYETHYL)FERROCENE WITH BIS(TRIPHENYLSILYL) CHROMATE

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

Stoichiometry and kinetics have been studied of the oxidation of (1-hydroxyethyl)ferrocene with bis(triphenylsilyl) chromate in benzene solutions at 20–45°C. The two compounds react at a molar ratio 1 : 1 to give acetylferrocene, a compound of Cr(IV) and mixture of triphenylsilanol with hexaphenyldisiloxane. A reaction mechanism is suggested and discussed.

Ferrocene and its derivatives undergo easy one-electron oxidation to give the respective ferricenium cation. Therefore, it is difficult to oxidize a substituent in ferrocene nucleus without a preferred attack of the latter. In a previous communication¹ it was shown that primary and secondary alcohols containing a ferrocenyl substituent can be selectively oxidized to the corresponding aldehydes and ketones with bis(triphenylsilyl) chromate (*I*) in organic non-polar solvents. Under these reaction conditions not even traces of ferricenium ion were observed.

The present communication summarizes results of investigation of stoichiometry and kinetics of reaction between bis(triphenylsilyl) chromate (*I*) and (1-hydroxyethyl)ferrocene (*II*) which represents one of the alcohols containing the ferrocene residue.

EXPERIMENTAL

Reagents. The compounds *I*, *II*, (1-deuterio-1-hydroxyethyl)ferrocene, triphenylsilanol, and hexaphenyldisiloxane were prepared according to refs^{1–4}. Benzene was purified and dried according to ref.⁵. All the experiments were carried out with exclusion of light.

Analytical. The content of *I* was determined spectrophotometrically (λ 350 nm, $\epsilon = 490 \text{ m}^2 \cdot \text{mol}^{-1}$), that of ferrocene derivatives was determined in the same way after removal of *I* by reaction with a 10% solution of hydrazine hydrate and chromatographical separation on an alumina column (acetylferrocene λ 455 nm, $\epsilon = 35 \text{ m}^2 \text{ mol}^{-1}$; *II* λ 435 nm, $\epsilon = 9.8 \text{ m}^2 \text{ mol}^{-1}$). Silicon content was determined gravimetrically as SiO_2 , the Cr(VI) content iodometrically, the Cr(III) and Fe content spectrophotometrically (as complexes with ethylenediaminetetraacetic acid⁶ and *o*-phenanthroline, respectively). The content of triphenylsilanol in its mixtures with

hexaphenyldisiloxane was determined as active hydrogen content⁷. The spectrophotometric measurements were carried out with a Specord UV VIS (Zeiss, Jena).

Identification of products. Acetylferrocene was identified by its melting point, IR spectra (400 to 4 000 cm^{-1} , KBr disc, Specord 75 IR (Zeiss, Jena)), and thin-layer chromatography (TLC) comparison of the sample with standard. Triphenylsilanol and hexaphenyldisiloxane were identified by their IR spectra (cm^{-1} , KBr disc; triphenylsilanol $\nu(\text{Si}-\text{O})$ 792, 812, $\nu(\text{O}-\text{H})$ 3 680; hexaphenyldisiloxane $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ 1 075, $\nu_{\text{s}}(\text{Si}-\text{O}-\text{Si})$ 520) (ref.⁸).

Chromatography. TLC and column chromatography with alumina (activity II according to Brockmann) were used for the analysis and separation, respectively. The eluents used for the ferrocene derivatives and for mixtures of triphenylsilanol with hexaphenyldisiloxane were benzene-diethyl ether 1 : 1 (v/v) and ethanol, respectively.

Oxidation. Mixture of 6.35 g (10 mmol) *I* and 2.30 g (10 mmol) *II* in 250 ml benzene was left to stand 24 h at 25°C. During this period the mixture gradually turned dark and separated a brown precipitate which was collected by suction, washed with benzene, and dried (yield 1.74 g). Composition of the precipitate: 28.29% Cr, 2.22% Si, 0.36% Fe. The precipitate partially dissolves in 0.5M sulphuric acid, and the solution contains 2.72 mmol Cr(VI) and 5.61 mmol Cr(III) (the ratio Cr(III) : Cr(VI) = 2.06); the undissolved residue (0.33 g) is a mixture of triphenylsilanol and hexaphenyldisiloxane. The mother liquor and wash benzene were combined and gave 2.16 g acetylferrocene (94.7%) and 5.11 g mixture containing triphenylsilanol (29%) and hexaphenyldisiloxane.

Kinetic measurements. The reaction kinetics were followed by time decrease of concentration of *I*. The reaction mixture was kept at a constant temperature, and samples were withdrawn at definite time intervals. Content of oxidizing agent in the samples was determined after removing the precipitate of the reduction product. The concentration values calculated from absorbances of solutions of the oxidizing agent at five various wavelengths within 345 to 400 nm do not differ within experimental error (2% rel.). The time needed for withdrawal and treatment of one sample did not exceed 200 s. During this time no significant absorbance changes of the sample take place.

RESULTS

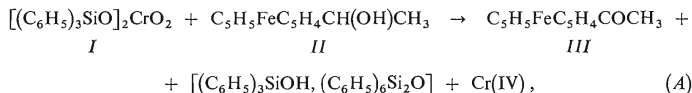
The only product of oxidation of *II* with *I* in benzene is acetylferrocene (*III*) which was isolated in 95% yield. In no reaction phase any other oxidation product of nucleus (ferricenium ion) or substituent of the sandwich molecule *II* was observed. A slight part (about 1%) of the substance is decomposed under the reaction conditions, which follows from the presence of "free" iron in the precipitate of the reduction product.

The final product of reduction of *I* consists of a mixture of triphenylsilanol and hexaphenyldisiloxane and insoluble (in the given system) precipitate containing an almost theoretical amount of chromium at average oxidation state of Cr(IV). Besides, the precipitate contains below 6% of $(\text{C}_6\text{H}_5)_3\text{Si}$ groups and traces of decomposition products of ferrocene nucleus (molar ratio Cr : Si : Fe \approx 81 : 12 : 1). No further information about this complicated reaction product could be obtained. Also it is not known why hexaphenyldisiloxane is formed beside triphenylsilanol.

Several papers dealing with oxidation of alcohols with esters of chromic acid^{9,10} formulate the reduction product as CrO_2 . We could not confirm this statement.

We cannot exclude the possibility that the precipitate isolated by us contains this substance beside a considerable amount of sorbed impurities.

The reaction stoichiometry was determined from ratios of the consumed oxidizing agent and acetylferrocene formed in the reaction. The benzene solutions were kept at 20–45°C for 0.5–24 h. The reaction mixture was rid of the reduction product precipitate by centrifugation, and concentrations of the oxidizing agent and acetylferrocene were determined in the solution. The results are given in Table I and can be summarized in the stoichiometric equation



where Cr(IV) means a compound (further not identified) of an average oxidation state of Cr(IV). Thus the compound *I* acts on *II* as a two-electron oxidizing agent. The stoichiometry 1 : 1 of the reaction components remains unchanged *a*) when changing the concentrations of the reactants within the limits $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mol \cdot l^{-1} (experiments 2, 8), *b*) when changing the reaction temperature within the limits 25 to 45°C (experiments 1, 2), *c*) when changing molar ratio of the reactants (experiments 6 to 8), *d*) in the whole reaction course (experiments 3 to 6). It was proved qualitatively (TLC) that the 1 : 1 stoichiometry of the reaction remains unchanged even in solutions with starting concentrations of components about 10^{-4} mol l^{-1} .

TABLE I

Consumption of bis(triphenylsilyl) chromate for oxidation of (1-hydroxyethyl)ferrocene

No	Initial concentration of <i>II</i> mol l^{-1}	Concentration of <i>I</i> mol l^{-1}		Concentration of <i>III</i> mol l^{-1}	Time h	Temperature °C	Ratio <i>I/III</i>
		initial	final				
1	$4 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	—	$3.79 \cdot 10^{-2}$	24	25	1.06
2	$4 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	—	$3.68 \cdot 10^{-2}$	6	45	1.09
3	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$5.70 \cdot 10^{-3}$	$4.50 \cdot 10^{-3}$	0.5	20	0.95
4	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$4.58 \cdot 10^{-3}$	$5.30 \cdot 10^{-3}$	1	20	1.03
5	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$0.98 \cdot 10^{-3}$	$8.60 \cdot 10^{-3}$	2	20	0.95
6	$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	—	$9.48 \cdot 10^{-3}$	24	20	1.06
7	$2 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$0.92 \cdot 10^{-4}$	$9.85 \cdot 10^{-3}$	6	25	1.09
8	$5 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	—	$4.85 \cdot 10^{-3}$	6	25	1.13

The studies of the reaction kinetics revealed that reciprocal value of concentration of I in equimolar mixtures of the components ($c_0 = 5 \cdot 10^{-4} \text{ mol l}^{-1}$) showed linear dependence on time (except for a slight induction period) up to more than 90% conversion. The reaction rate obeys the relation

$$-d\{I\}/dt = k_{\text{obs}}\{I\}^2, \quad (1)$$

where $\{ \}$ denotes concentrations of the compounds, $t =$ time. The k_{obs} values calculated from linear dependences $1/k_{\text{obs}}$ vs t for various temperatures are as follows:

Temperature, °C	20	25	30	35	40	45
$k_{\text{obs}}, \text{l mol}^{-1} \text{ s}^{-1}$	0.13	0.18	0.22	0.30	0.41	0.49

The time dependence of the ester concentration follows the second order equation also in mixtures containing I at the starting concentration $5 \cdot 10^{-4} \text{ mol l}^{-1}$ and II at variable starting concentrations (0.2 to $1 \cdot 10^{-3} \text{ mol l}^{-1}$). Table II summarizes the rate constants k_{obs} calculated from the relation

$$k_{\text{obs}} \cdot t = 1/(a - b) \ln(a - x)/(b - x) - \ln a/b, \quad (2)$$

TABLE II

Rate constants (k_{obs}) for systems with non-stoichiometric ratios of initial concentrations of bis-(triphenylsilyl) chromate ($c = 5 \cdot 10^{-4} \text{ mol l}^{-1}$) and (1-hydroxyethyl)ferrocene

Initial concentration of II $\text{mol l}^{-1} \cdot 10^3$	$k_{\text{obs}}, \text{l mol}^{-1} \text{ s}^{-1}$	
	20°C	40°C
1.0	0.14	0.42
0.9	0.13	0.46
0.8	0.13	0.46
0.7	0.15	0.49
0.6	0.11	0.49
0.5	0.13	0.41
0.4	0.12	0.51
0.3	0.12	0.52
0.2	0.10	0.50

where a , b are the initial concentrations of the components, x is decrease of oxidizing agent. The k_{obs} constants obtained with systems containing various initial concentrations of the components do not much differ, showing a random scattering. Average values of the k_{obs} constants are 0.13 ± 0.02 (20°C) and 0.47 ± 0.04 (40°C). Thus the reaction follows the kinetic equation of 2. order, being first order in each: oxidizing agent and alcohol.

$$-d\{I\}/dt = k_{\text{obs}}\{I\}\{II\} \quad (3)$$

Addition of hexaphenyldisiloxane up to concentration $1 \cdot 10^{-2} \text{ mol l}^{-1}$ has no effect on the reaction rate within experimental error. Also no change in the reaction rate was observed in the systems to which various amounts of the reduction product were added at the beginning. On the contrary, the solutions containing triphenylsilanol reacted more slowly, the rate decrease being proportional to concentration of the added substance. This effect of triphenylsilanol on the k_{obs} values can be expressed by Eq. (4):

$$1/k_{\text{obs}} = k_a\{(\text{C}_6\text{H}_5)_3\text{SiOH}\} + k_b \quad (4)$$

$k_a = 1\,400 \text{ s}$ (20°C) and $1\,040 \text{ s}$ (40°C), $k_b = 7.0 \text{ mol s l}^{-1}$ (20°C) and 1.8 mol s l^{-1} (40°C). Thus the complete rate equation reads

$$-d\{I\}/dt = \{I\}\{II\}/(k_a\{(\text{C}_6\text{H}_5)_3\text{SiOH}\} + k_b). \quad (5)$$

The oxidation rate of (1-deuterio-1-hydroxyethyl)ferrocene with I without addition of initial triphenylsilanol did not differ (within experimental error) from that of the non-deuterated substance. In systems containing initial $1 \cdot 10^{-2} \text{ mol l}^{-1}$ triphenylsilanol the oxidation rate of the deuterated substance was markedly lower. Table III gives the rate constant ratios $k_{\text{obs}}(^1\text{H}) : k_{\text{obs}}(^2\text{H})$.

Dependence of the rate constants on the reaction temperature fits well the Arrhenius relation. From the dependence of k_{obs} on temperature we calculated the activation parameters (25°C):

$$\Delta H^\ddagger = 36.6 \pm 6.2 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S^\ddagger = -60.3 \pm 9.3 \text{ J mol}^{-1} \text{ K}^{-1}.$$

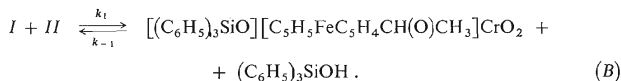
DISCUSSION

Oxidation of primary and secondary alcohols with compounds of hexavalent chromium to the corresponding carbonyl compounds gives only exceptionally such high yields as in the case studied. Very often (even when applying the chromate esters) C—C bond splitting takes place to give side products which in some cases can predominate¹¹. However, I acts as a gentle selective oxidizing agent even on very sensitive II . Mechanism of oxidation of alcohols with compounds of hexavalent chro-

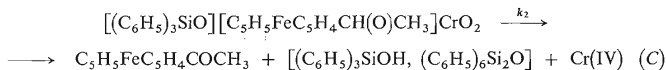
mium is known in considerable detail. All available data can be explained by a mechanism suggested by Westheimer, Roček and Trahanovsky¹². This mechanism postulates a two-step process: the first one consists in formation of ester of chromic acid and the alcohol being oxidized, the second step represents a redox decomposition of the intermediate to give the carbonyl compound and chromium compound at a formal oxidation level Cr(IV). The latter is either final product (in non-polar media) or it oxidizes another portion of alcohol or its primary oxidation products (acid media).

In most cases the first step (the equilibrium esterification) was found to be faster than the second step (the irreversible redox decomposition) which is thus rate limiting. Opposite ratio of the two reaction rates was observed in two cases in which sterical or electrostatic effects slowed down the esterification rate to such extent that this step became rate limiting^{13,14}.

The results obtained by us generally agree with the mentioned mechanism. The first reaction step consists in an equilibrium transesterification (its reaction rate is markedly influenced by concentration of the product — triphenylsilanol).



This step is followed by irreversible decomposition of the intermediate.



The compound Cr(IV) is insoluble in the reaction system and does not take part in any further reaction.

TABLE III

Deuterium kinetic factors $k_{obs}(^1H) : k_{obs}(^2H)$

Temperature, °C	20	25	30	35	40
The factor for $c = 0^a$	0.96	0.98	1.06	0.94	1.08
The factor for $c = 1 \cdot 10^{-2}^a$	2.03	—	1.89	—	2.06

^a c Initial concentration of $(C_6H_5)_3SiOH$ in $mol\ l^{-1}$.

However, it seems possible that in the system studied by us the both alternatives of the rate-limiting step can make themselves felt: 1) In the cases without added triphenylsilanol the rate-limiting step consists in the relatively slow (non-catalyzed) transesterification. This result also agrees with the value of kinetic deuterium factor $k_{\text{obs}}(^1\text{H}) : k_{\text{obs}}(^2\text{H})$ close to 1. 2) In the cases with great excess of triphenylsilanol the equilibrium (B) is established much more quickly, but it is markedly shifted to the left. The reaction is slowed down to such extent that the second step (irreversible redox decomposition) becomes rate limiting. This is confirmed by the value of kinetic deuterium factor $k_{\text{obs}}(^1\text{H}) : k_{\text{obs}}(^2\text{H}) \sim 2$.

The reaction scheme following from the Eqs (B) and (C) cannot be solved exactly in the closed form. If, however, a simplification is adopted that the rates of the two steps are sufficiently different, then two alternatives are possible ($k_2 \gg k_1$ and $k_1 \gg k_2$) which can be solved.

For the first case $k_2 \gg k_1$ it is

$$-d\{I\}/dt = k_1 k_2 \{I\} \{II\} / (k_{-1} \{(C_6H_5)_3SiOH\} + k_2). \quad (6)$$

The rate equation (5) obtained from our experiments is formally identical with Eq. (6) when $k_a = k_{-1}/k_1 k_2$ and $k_b = 1/k_1$. The k_{obs} constant is thus connected with the constants of the scheme by the relation

$$k_{\text{obs}} = k_1 k_2 / (k_{-1} \{(C_6H_5)_3SiOH\} + k_2). \quad (7)$$

When evaluating the experiments carried out without added triphenylsilanol it is possible to neglect (within experimental error) the term $k_{-1} \{(C_6H_5)_3SiOH\}$ with respect to k_2 . Then Eq. (7) is reduced to:

$$k_{\text{obs}} = k_1. \quad (8)$$

In the presence of a great excess of triphenylsilanol, on the contrary, the situation $k_{-1} \{(C_6H_5)_3SiOH\} \gg k_2$ can result, and Eq. (7) will be transformed to

$$k_{\text{obs}} = k_1 k_2 / k_{-1} \{(C_6H_5)_3SiOH\} = K k_2 / \{(C_6H_5)_3SiOH\}, \quad (9)$$

where K means the equilibrium constant of the transesterification. It can be noted that a formally identical relation would also result, if the reaction scheme were solved for the case $k_1 \gg k_2$.

Forms of Eqs (8) and (9) correspond to courses of the kinetic curves and to values of kinetic deuterium factors. The splitting of C—¹H (or C—²H) bond is involved in the process characterized by the constant k_2 . Therefore, in the experiments ful-

filling Eq. (8) the observed kinetic deuterium factor has a value close to 1, whereas in the cases described by Eq. (9) it reaches a higher value (~ 2).

Thus on the basis of our results the course of the reaction of *I* with *II* can be explained fully by the idea of two-step reaction in which transesterification reaction of the initial components is followed by a redox decomposition of the intermediate ester. However, both the transesterification and the redox decomposition are probably more complicated processes. The values of activation parameters and kinetic deuterium factors do not exclude an idea that the transesterification proceeds through a transition state having an increased coordination number at the chromium atom, and that the proper redox process is accomplished in a cyclic mechanism, which fully agrees with the scheme given in ref.⁹.

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