

OXIDATION OF (1-HYDROXYBENZYL)FERROCENE AND ITS DERIVATIVES SUBSTITUTED IN PHENYL RING WITH BIS(TRIPHENYLSILYL) CHROMATE

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Kinetics have been studied of oxidation of (1-hydroxybenzyl)ferrocenes substituted in phenyl ring with bis(triphenylsilyl) chromate in benzene solutions as well as protonation of these alcohols in sulphuric acid medium. Logarithms of the oxidation rate constants (k_{obs} , 20–40°C) and those of the protonation equilibrium constants (K_{R^+} , 25°C) show linear dependence on the Hammett σ constants, the ρ constant values being -0.86 to -0.40 and -2.50 , respectively. These negative values suggest that the both processes are influenced by the same effects and confirm the mechanism proposed earlier for oxidation of alcohols with ferrocenyl substituent by action of bis(triphenylsilyl) chromate in aprotic solvents.

Our previous communications^{1,2} proved a possibility of oxidation of primary and secondary alcohols containing ferrocenyl substituent by action of bis(triphenylsilyl) chromate to give the corresponding aldehydes and ketones without competing attack at the ferrocene nucleus, and the reaction conditions were described under which this reaction can be carried out selectively and with high yields. In the study² the model example of oxidation of (1-hydroxyethyl)ferrocene with bis(triphenylsilyl) chromate in benzene was used for elucidation of stoichiometry and kinetics of this reaction and for suggestion of its possible mechanism. This mechanism can be formulated as a variant of so called esterification mechanism with the rare feature of the first reaction step being rate limiting (in our case: transesterification equilibrium reaction of the ferrocene alcohol and bis(triphenylsilyl) chromate) and followed by irreversible decomposition redox reaction of the ester.

To confirm these ideas, we have now studied under the same reaction conditions the oxidation of (1-hydroxybenzyl)ferrocene (*I*) and some its derivatives substituted in phenyl ring, *i.e.* substances of general formula $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}(\text{OH})\text{R}$, where R means 4-(CH_3)₃CC₆H₄ (*II*), 4-CH₃OC₆H₄ (*III*), 4-ClC₆H₄ (*IV*), and 3,4-Cl₂C₆H₃ (*V*). The same oxidation was also applied to the derivatives *I–V* deuterated at C₍₁₎ atom (*i.e.* the carbon atom carrying the hydroxyl group). For comparison, the paper also includes results of protonation study of the said (1-hydroxybenzyl)ferrocenes in sulphuric acid.

EXPERIMENTAL

Reagents. Preparation, purification, and identification of the compounds *I* to *V* and bis(triphenylsilyl) chromate were described in our previous communication¹. The substances deuterated at C₍₁₎ atom (*i.e.* those with —CD(OH)—grouping) were prepared by the procedure given in ref.¹: reduction of the corresponding ketones with LiAlD₄. Isotopic purity of the substances varied within 95 to 97 per cent.

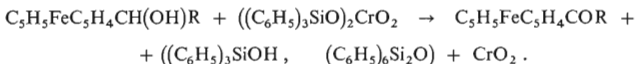
Kinetic measurements. All the kinetic measurements based on the decrease of bis(triphenylsilyl) chromate with time were carried out in the way given in ref.². Each rate constant was obtained from three independent measurements, in which the starting reaction mixtures contained equimolar amounts of the alcohol and oxidant (in the concentration range $3 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ mol \cdot l⁻¹) and no triphenylsilanol. Error of the measurements (standard deviation) did not exceed 1% rel. The activation parameters were determined from precisely linear dependence of logarithm of quotient of rate constant and temperature *vs* reciprocal temperature in the region 20 to 40°C.

Measurement of protonation constants. For this purpose were used spectrophotometric procedures of ref.³, acidity of the sulphuric acid solutions being evaluated with the use of the *I*₀ scale defined by Gold and Hawes⁴.

RESULTS

Oxidation of Alcohols I–V with Bis(triphenylsilyl) Chromate in Benzene

In the first step it was proved experimentally that the both reaction components react in molar ratio 1 : 1. Hence, in analogy to the model system² the oxidation stoichiometry can be described with the equation:



Also the reaction kinetics obeys formally identical equations under the same conditions. The equation for the reaction velocity (*v*) is first order in each of the reaction components:

$$v = k_{\text{obs}}[\text{alcohol}][\text{oxidant}],$$

the rate constant being inversely proportional to concentration of triphenylsilanol:

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

The rate constants *k*_{obs} are distinctly affected by nature of the substituent R in phenyl ring of the alcohol oxidized. The electron-withdrawing substituents (compounds *IV* and *V*) decrease the reaction rate, whereas the electron-donor substituents (compounds *II* and *III*) accelerate the reaction. The measured *k*_{obs} values (temperature

range 20–40°C) and deuteration isotopic kinetic factors of the reaction are summarized in Table I. The reaction rate constants fulfil well the Hammett equation: the $\log k_{\text{obs}}$ vs σ dependences are linear. Their slopes (ρ) are given in Table III along with the standard deviations (s) and regression coefficients (r). The oxidation rates of the $C_{(1)}$ -deuterated substances show no marked difference from those of the corresponding non-deuterated compounds. The small differences given in Table I as $k_{\text{obs}}(\text{H})/k_{\text{obs}}(\text{D})$ quotients cannot be considered significant.

Also the activation parameters of the reaction (Tables II and III) show good linear dependence on the Hammett constants, which is particularly true of the ΔG^\ddagger quantity. This fact alone indicates fulfilment of the condition of isokinetic relation⁵. The isokinetic temperature β was determined directly from the dependence $\log k_{\text{obs}}$ vs $1/T$, and it equals to $54 \pm 5^\circ\text{C}$. The value β found from the linear dependence ΔH^\ddagger vs ΔS^\ddagger ($\beta \approx 30^\circ\text{C}$) is obviously erroneous, since the dependences $\log k_{\text{obs}}$ vs $1/T$ (Table I) do not intersect in the whole region measured.

Protonation of Alcohols I–V in Sulphuric Acid

In sulphuric acid medium the alcohols I–V undergo equilibrium protonation followed immediately by formation of stable carbocation:

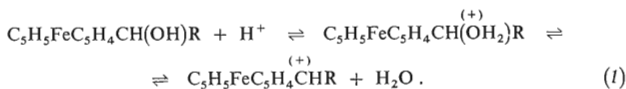


TABLE I

Rate constants (k_{obs}) and deuteration kinetic isotopic factors of oxidations of I–V with bis-(triphenylsilyl) chromate

Compound	$k_{\text{obs}}, \text{l mol}^{-1} \text{s}^{-1}$					$k_{\text{obs}}(\text{H})/k_{\text{obs}}(\text{D})$
	20°C	25°C	30°C	35°C	40°C	
I	0.120	0.158	0.194	0.263	0.331	1.02 ^a
II	0.149	0.184	0.229	0.275	0.354	0.98 ^b
III	0.194	0.234	0.275	0.339	0.380	1.08 ^b
IV	0.066	0.091	0.141	0.208	0.281	1.08 ^b
V	0.036	0.053	0.082	0.117	0.168	1.03 ^b

^a Mean value of five measurements (20–40°C); ^b at the temperature 25°C.

The protonation constants K_{R^+} defined by this equilibrium were calculated from the relation:

$$-I_0 = pK_{R^+} + \log \left(\frac{[C_5H_5FeC_5H_4CHR^{(+)}]}{[C_5H_5FeC_5H_4CH(OH)R]} \right). \quad (2)$$

Tables II and III give the K_{R^+} values and parameters of linear correlation $\log K_{R^+}$ vs σ , respectively.

TABLE II

Activation parameters of oxidation of *I-V* with bis(triphenylsilyl) chromate and protonation constants of *I-V*

Compound	ΔG^\ddagger kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	pK_{R^+}	K_{R^+} l mol ⁻¹
<i>I</i>	78.3 ± 1.7	36.2 ± 1.2	-138.8 ± 3.9	-0.42 ± 0.01	2.7
<i>II</i>	78.0 ± 1.4	30.0 ± 1.0	-158.4 ± 3.3	-0.52 ± 0.02	3.3
<i>III</i>	77.5 ± 1.4	23.7 ± 1.0	-177.7 ± 3.5	-1.46 ± 0.08	29.4
<i>IV</i>	79.3 ± 2.5	54.3 ± 1.8	-82.3 ± 6.1	-0.12 ± 0.02	1.3
<i>V</i>	80.7 ± 1.3	56.6 ± 0.9	-79.5 ± 3.1	1.01 ± 0.13	0.1

TABLE III

Parameters of linear correlations of the Hammett dependences (σ_p)^{a,b} of the quantities $\log k_{obs}$, ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and pK_{R^+}

Quantity	ρ	s^c	r^d
$\log k_{obs}$ (20°C)	-0.86	0.04	0.996
$\log k_{obs}$ (25°C)	-0.76	0.05	0.995
$\log k_{obs}$ (30°C)	-0.60	0.01	0.999
$\log k_{obs}$ (35°C)	-0.51	0.05	0.985
$\log k_{obs}$ (40°C)	-0.40	0.06	0.973
ΔG^\ddagger	3.69	0.17	0.997
ΔH^\ddagger	40.4	8.2	0.943
ΔS^\ddagger	121.4	27.2	0.932
$\log K_{R^+}$	-2.50	0.40	0.962

^a Ref.⁵; ^b for compound *V* the sum ($\sigma_p + \sigma_m$), ref.⁵; ^c standard deviation; ^d correlation coefficient.

DISCUSSION

Oxidation of alcohols to carbonyl compounds involves removal of a C—H bond (here $C_{(1)}-H$). The form of kinetic equation for the oxidation of the compounds $I-V$ with bis(triphenylsilyl) chromate in aprotic medium and the values of deuterium kinetic isotopic factors are inconsistent with the redox reaction being rate-limiting. On the contrary, these findings agree with the mechanism suggested in our previous communication²: the rate-limiting step is the transesterification reaction between the alcohol and oxidant, whereafter there follows the irreversible redox reaction. Negative value of the Hammett ρ constant in the relation $\log k_{obs}$ vs σ means increase of the reaction rate with increasing electron density at the reaction centre of the substrate. This effect is favourable for the first reaction step (transesterification) and, on the contrary, unfavourable for the second reaction step (redox reaction) which requires, for easier hydrogen-transfer, lowering of electron density at the reaction centre. Finally, the same sign of the ρ values of oxidation velocities and protonations of the group of alcohols in the studied temperature interval indicates that the two processes are similarly affected by substituents. This fact agrees with the presumption that the protonation starts with addition of the proton to oxygen atom of hydroxyl group of the alcohol, and the oxidation of the alcohol starts with similar addition of positively charged centre of the oxidant (chromium atom at the VI oxidation level):



Thus, according to this idea, the transesterification goes *via* the transition state having increased coordination number at the chromium atom ($A_{Ac}2$ mechanism). The rate-limiting step consists in nucleophilic addition of the alcohol to the central chromium atom of the oxidant molecule, which agrees with relatively low values of activation entropies.

However, it cannot be excluded that, at higher temperatures (above isokinetic point $\sim 54^\circ\text{C}$), the sequence of the two processes (transesterification and redox decomposition) is changed. Similar change in mechanism due to dependence of the reaction rate on concentration of one reaction product (triphenylilanol) was observed earlier². However, experimental verification of such idea is difficult and was unsuccessful so far, since it requires to carry out kinetic measurements at the temperatures at which the system shows anomalous behaviour as a consequence of non-negligible participation of side reaction (oxidation decomposition of sandwich structure of ferrocene nucleus). The changed sequence of the two reactions should be connected with a higher value of the kinetic deuterium factor ($k_{obs}(\text{H})/k_{obs}(\text{D}) \approx 2$ and above)². In the investigated temperature interval, however, no distinct increase of values of this factor could be observed which could support the above-mentioned idea.

REFERENCES

1. Holeček J., Handlíř K., Klikorka J., Nádvorník M.: *J. Prakt. Chem.* **324**, 345 (1982).
2. Holeček J., Handlíř K., Nádvorník M.: *This Journal* **47**, 562 (1982).
3. Cerichelli G., Floris B., Ortagi G.: *J. Organometal. Chem.* **78**, 241 (1974).
4. Gold V., Hawes B. W.: *J. Chem. Soc.* **1951**, 2102.
5. Exner O.: *Korelační vztahy v organické chemii*, p. 74. Published by SNTL/Alfa, Prague 1981.

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