

THE SPECTRA OF ESTERS OF OXOHYDROXOBIS-
 -(8-HYDROXY-QUINOLINE)VANADIUM(V)

(Short communication)

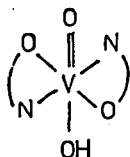
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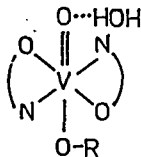
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The vanadate ion reacts with 8-hydroxyquinoline in aqueous solution at $\text{pH} \approx 6$ to give a stable complex compound, I-H [1] (Structure 1). BIELIG and BAYER [2] confirmed the presence of the OH group *via* the IR spectrum; this result, together with the analytical data, leads to the formula $(\text{C}_9\text{H}_6\text{ON})_2\text{VO}\cdot\text{OH}$. This complex dissolves in alcohols to give hydrated esters, I'-R (Structure 2) in the first step; in an excess of boiling aliphatic alcohols I'-R next gives intense red solutions [3], from which red crystals of the anhydrous esters, I-R (Structure 3), separate out on cooling.



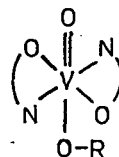
I - H

Structure 1



I' - R

Structure 2



I - R

Structure 3

I-H deposits slowly from concentrated solution of I-R; the solubility of I-R and its tendency to undergo decomposition increase with increasing C atom number in R.

We have prepared the compounds I-H, I'-R and I-R (R = methyl, ethyl, propyl, butyl, amyl, hexyl and octyl) and measured their visible and UV spectra in the corresponding parent n-alcohols and pyridine (py). The spectra were obtained on BECKMAN DU, SPECORD UV-VIS instruments, using spectroscopically pure solvents.

The central V^{5+} ion is a $3d^0$ species, and the complex I-H is diamagnetic [2b]; no d-d bands are expected, and none are observed. The complexes I-H and I-R all give five bands of high intensities (Table I). The bands in the range 240–370 nm are modified bands of 8-hydroxyquinoline due to $\pi^* \leftarrow \pi$ transitions, while the visible band (≈ 490 nm) may be assigned to ligand-to-metal charge-transfer transitions from the phenolate oxygens to the empty d-orbitals of the vanadium (Fig. 1) [4]. Such

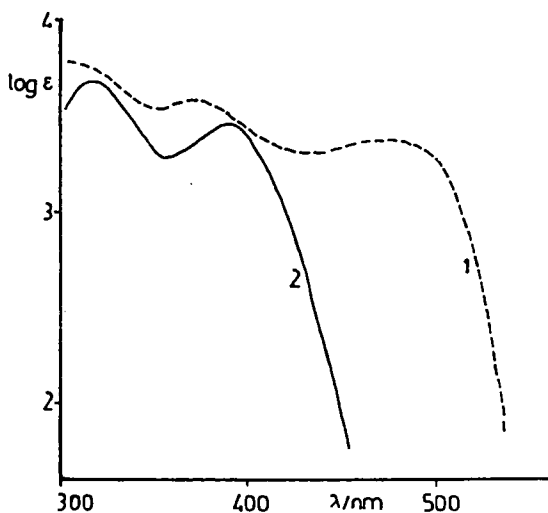


Figure 1:

Absorption spectra of I-C₂H₅
in ethanol(1) and pyridine(2)
 $c = 3 \cdot 10^{-4}$ mol/dm³,
 $d = 0.1$ cm.

transitions are generally characteristic of phenolate coordination to easily reducible metal ions [5].

It has been reported [6] that the reactions between I-H and aliphatic alcohols result in hydrated esters, I'-R, containing a molecule of water attached by hydrogen-bonding. In excess of boiling alcohol, which may well act as a mild dehydrating agent, the compounds I'-R are transformed to anhydrous esters I-R as final products. In the IR spectra of I-R, no hydroxyl frequencies are observed [6]. For a discussion of the mechanism of ester formation, see *e.g.* [6]. The absorption spectra of the hydrated and the anhydrous compounds are practically the same. Table I shows that the spectra of the red products dissolved in the parent alcohols vary slightly as group R changes from CH₃ to C₈H₁₇; the visible band shifts somewhat hypsochromically and the intensities increase in the sequence CH₃ → C₈H₁₇.

Table I

Spectral data on the compounds I-R measured in the parent alcohols ROH and pyridine

R =	λ/nm and $(\log \epsilon)$							
	in alcohols				in pyridine			
CH ₃	490(2.95)	367(3.58)	315(3.71)	256(4.44)	240(4.72)	388(3.50)	310(3.73)	
C ₂ H ₅	485(3.35)	366(3.56)	310(3.73)	256(4.36)	242(4.72)	390(3.49)	310(3.72)	
C ₃ H ₇	485(3.49)	376(3.65)	312(3.76)	260(4.30)	243(4.76)	387(3.49)	310(3.71)	
C ₄ H ₉	480(3.44)	370(3.63)	310(3.75)	260(4.34)	242(4.68)	392(3.51)	315(3.74)	
C ₅ H ₁₁	480(3.52)	372(3.69)	310(3.78)	260(4.35)	242(4.71)	396(3.48)	315(3.72)	
C ₆ H ₁₃	480(3.58)	372(3.65)	312(3.80)	260(4.32)	242(4.68)	392(3.45)	313(3.72)	
C ₈ H ₁₇	478(3.60)	374(3.70)	312(3.78)	262(4.30)	242(4.70)	392(3.48)	312(3.72)	

When I-CH₃ is dissolved in propanol, for example, and I-C₃H₇ in methanol, we obtain the same spectra as when I-C₃H₇ is dissolved in propanol or I-CH₃ in methanol; consequently, in the presence of a large excess of the other alcohol, a transesterification takes place. When the complexes I-CH₃ - I-C₈H₁₇ are dissolved

in mixtures of two different alcohols, an equilibrium system forms; the calculated equilibrium constants are between $2 \cdot 10^{-2}$ and $9 \cdot 10^{-2}$, and ΔH varies between 8.5 and 17.5 kJ mol⁻¹ [7].

Dissolution of the hydrated esters, I'-R, in py results in yellow solutions. The final spectra are the same for all the complexes, with two characteristic bands at 390 nm ($\log \epsilon = 3.50$) and 310 nm ($\log \epsilon = 3.72$). The red \rightarrow yellow transformation of the solutions may be followed well spectrophotometrically. From py solutions, yellow crystals can be isolated, the analytical data on which suggest the presence of two py molecules; on heating, two py molecules are released. The IR spectra of the yellow final products contain $\nu_{\text{V}}=0$ and ν_{OH} frequencies at 948 and 3440 cm⁻¹, respectively. The compounds I-H and I'-R yield the same final products.

The spectrophotometric measurements indicate that in py solution, where the py is both a solvent and a reactant, a pseudo-first-order reaction takes place. The rate constants and the calculated thermodynamic parameters are presented in Table II.

Table II

The pseudo-first-order rate constants and the calculated thermodynamic parameters on the reaction of I'-R and pyridine

R =	$k'/10^4 \text{ s}^{-1}$			E_a	ΔH^*	$-\Delta S^*$
	298 K	308 K	318 K	kJ·mol ⁻¹	kJ·mol ⁻¹	J·K ⁻¹ mol ⁻¹
CH ₃	5.22	11.31	21.48	55.79	53.23	129.00
C ₂ H ₅	3.91	8.19	17.16	58.30	55.74	123.16
C ₃ H ₇	1.90	4.84	11.24	70.03	67.47	89.68
C ₄ H ₉	1.98	4.89	10.34	65.17	62.61	105.55
C ₅ H ₁₁	1.75	4.61	9.74	67.72	65.16	97.94
C ₆ H ₁₃	1.72	4.53	9.39	66.98	64.42	100.54
C ₈ H ₁₇	1.67	4.53	9.15	67.11	64.55	100.27

The data show that the rate constants decrease in the sequence $C_1 \rightarrow C_5$; for higher alcohols, no further significant change in the reaction rate is observed. The ARRHENIUS activation energy, E_a , and the enthalpy of activation, ΔH^\ddagger , increase from $I-CH_3$ to $i-C_5H_{11}$. The parameters for $I-C_3H_7$ differ strongly from the expected ones. The high negative values of the activation entropy, ΔS^\ddagger , are noteworthy. The activation parameters vary with the number of carbon atoms, n , according to a zig-zag shape, similarly to the changes in other parameters in the homologous series. On the other hand, a plot of ΔH^\ddagger vs. ΔS^\ddagger results in a linear correlation ($r = 0.997$).

The mechanism of the reaction is problematic. We consider the following mechanism to be possible. On dissolution in py, the HOH molecule and the R group split off to result in $I-H$. Then, one of the $V-O$ bonds opens and one py molecule, which has a high coordinating ability, is coordinated directly to the central V^{5+} via its lone pair electrons. This step is very fast and results in a positive charge on the central ion. The intermediate reacts with a further py molecule more slowly, because the charge on the central ion makes further $V-O$ bond-breaking more difficult. This second step takes place with measurable rate, according to the equation

$$\text{rate} = k[I^+-R][py].$$

Since $[py]$ in py solution is about $12.573 \text{ mol dm}^{-3}$, which is much higher than $[I^+-R]$, the reaction takes place as a pseudo-first-order reaction, and we may use the equation

$$\text{rate} = k'[I^+-R].$$

Table II presents the $k' = k/12.573$ values. If we consider that the charged activated complex is formed from two molecules (I^+-R and one py molecule), that the final product has a still higher charge, and that the py molecules have a high polarization effect, the highly negative activation entropy values are obvious [8].

References

- [1] *Montequi, R., M. Gallego: Ann. Soc.esp.Fis.Quim., 32, 134 (1934).*
- [2] (a) *Bielig, H.J., E. Bayer: Liebigs Ann., 584, 96 (1953).*
(b) *Bayer, E., H.J. Bielig: Liebigs Ann., 584, 116 (1953).*
- [3] *Bach, J.M., R.A. Trelles: An.Assoc.quim.argen., 28, 111 (1940).*
- [4] *Bonadies, J.A., C.J. Carrano: J.Amer.Chem.Soc., 108, 4088 (1986).*
- [5] *Patch, M.G., C.J. Carrano: Inorg.Chim.Acta, 56, 171 (1981).*
- [6] *Blair, A.J., D.A. Pantony, G.J. Minkoff J.Inorg.Nucl.Chem., 5, 316 (1958).*
- [7] *Császár, J., J. Balog: Acta Phys. et Chem. Szeged, 6, 33 (1959).*
- [8] *Pearson, R.G.: J.Chem.Phys., 20, 1478 (1952).*