

The relative high yields of 1,2-diarylethanol obtained by reacting nitrotoluenes with benzaldehydes (runs 2-6) are in contrast to the results of Russell and Becker.⁶ They reacted aromatic aldehydes with aryl compounds containing active methyl groups and isolated only the corresponding stilbenes. Their reactions were run with more than 100 mole % of base, and this is probably one reason for their high yield of the elimination product (see below).

When 2-nitrotoluene and formaldehyde were reacted with larger amounts of base present, three products were isolated in addition to 2-(2-nitrophenyl)ethanol: sodium formate, methanol, and 2-nitrostyrene. The presence of the two first of these products shows that a Cannizzaro reaction competes with the addition of nitrotoluene to the aldehyde. In the case of nitrotoluene and formaldehyde, the latter reaction is favoured in the competition. However, when 2-nitrotoluene was reacted with the highly reactive 4-nitrobenzaldehyde in DMSO with sodium ethoxide as base, only 4-nitrobenzyl alcohol was isolated together with 4-nitrobenzoic acid, showing the Cannizzaro reaction to be the favoured one in that case.

The 2-nitrostyrene is probably formed from 2-(2-nitrophenyl)-ethanol by a base-catalysed elimination of water. 2-(2-Nitrophenyl)ethanol is stable towards elimination under acidic conditions: After 30 min of reflux with 10 % aqueous H_2SO_4 , only starting material (80 %) was isolated.

Attempts to add the nitrotoluenes to aliphatic aldehydes as acetaldehyde or butyraldehyde under these conditions have all failed, due to the rapid aldol condensation of the aldehyde. The addition of 2- and 4-mononitrotoluenes to aldehydes is thus restricted to aldehydes without α -hydrogen atoms and to aldehydes whose Cannizzaro reaction does not compete too well with the nitrotoluene for the base.

The reaction is under further investigation.

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1. Wesslén, B. *Acta Chem. Scand.* **21** (1967) 718.
2. Bakke, J. Presented before »Svenska Kemistsamfundets Organikerdaggar», June 14-16, 1967, Gothenburg, Sweden.

3. Pfeiffer, P. and Monath, J. *Ber.* **39** (1906) 1304.
4. Thiele, J. and Escales, R. *Ber.* **34** (1901) 2842.
5. Martin, D., Weise, A. and Niclas, H.-J. *Angew. Chem.* **79** (1967) 340.
6. Russell, G. A. and Becker, H.-D. *J. Am. Chem. Soc.* **85** (1963) 3406.

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Equilibrium Studies of Polyanions

15. Vanadates in the "Instability Range" at 40°C

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In 1956 Rossotti and Rossotti¹ published an emf study on vanadates in the acidic ionic medium 1 M (H^+ , Na^+) ClO_4 in which z , the average charge per vanadium atom, and B , the total (analytical) concentration of vanadium, were varied as follows: $+1 \geq z \geq -1.6$ and $0.0025 M \leq B \leq 0.0200 M$. They could explain their data assuming that the ion VO_2^+ , on decreasing $[H^+]$ forms the complexes $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$.

Later on Brito and Ingri² studied the behavior of vanadates in the alkaline medium 0.5 M $Na(Cl^-, OH^-)$ covering the range $-1 \geq z \geq -2$ and $0.6 mM \leq B \leq 80 mM$. Using graphical methods they could explain their data assuming the species HVO_4^{3-} , $HV_2O_7^{3-}$, $V_3O_9^{3-}$, and VO_3^- . However, recent calculations³ of the same data using Letagropvrid⁴ indicate that a still better fit is obtained by adding the complexes $V_2O_7^{4-}$, $V_4O_{13}^{6-}$, and $V_4O_{12}^{4-}$; this reduces $\sigma(z)$, the standard deviation, from 0.012 (for 4 species) to 0.009 (for 7 species). Thus it seems that the metavanadates ($z = -1$) are both tri- and tetranuclear.

The present note concerns a similar study carried out a few years ago at 40°C with 0.5 M $Na(Cl)$ medium, in which B ranged from 0.018 M to 0.100 M and z

Table 1.

(p,q)	log K _{pq}				
(0,3)	7.11 ± 0.10	7.14 ± 0.01	7.23 ± 0.06	7.29 ± 0.04	7.30 ± 0.08
(0,4)	10.15 ± 0.11	10.10 ± 0.08	10.06 ± 0.10	10.10 ± 0.08	9.98 ± 0.12
(5,10)	57.57 ± 0.15	57.42 ± 0.16	57.44 ± 0.20	58.38 ± 0.09	57.34 ± 0.16
(6,10)	61.81 ± 0.13	61.81 ± 0.15	61.83 ± 0.14	61.56 ± 0.18	≈ 60.2 (< 61.5)
(3,6)		33.04 ± 0.01	33.15 ± 0.04	33.22 ± 0.11	33.24 ± 0.14
(5,9)			53.33 ± 0.07	53.73 ± 0.14	≈ 53.9 (< 54.0)
(2,1)				8.62 ± 0.18	≈ 8.3 (< 8.9)
(6,9)					≈ 57.3 (< 57.6)
σ(Z)	0.0067	0.0047	0.0043	0.0039	0.0038

changed from -0.6 to -1.0. The z range studied covered z values between the previous studies on vanadates carried out in this laboratory.^{1,2} Due to the slow establishment of the equilibrium at 25°C, this range was called the "instability range".

Keeping B constant for each titration, h was measured by means of the cell,

Ag, AgCl/0.5 M NaCl, sat. with AgCl/0.5 M NaCl/(equilibrium solution)/glass electrode

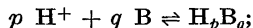
arranged as described elsewhere.⁵

The equilibrium at 40°C was reached after a certain period of time, which increased when z came close to $z = -1$, as follows: 5-10 min between $z = -0.4$ and $z = -0.6$; 20-35 min from $z = -0.6$ to $z = -0.9$; and finally, 1-2 h in the range $-0.9 < z \leq -1.0$.

If H represents the analytical excess concentration of H^+ , assuming the vanadium as HVO_3 , z is calculated from ($h = [H^+]$).

$$z = (h - H - K_w h^{-1})/B$$

In the present equilibrium calculations, H^+ ($= \bar{H}$) and VO_3^- ($= B$) were considered as the reagents, and hence Z ($= z - 1$) was defined as the average number of H^+ bound per VO_3^- . Therefore, assuming as usual that the activity factors are constant,⁶ the equilibrium constant K_{pq} for the formation of the (p,q) complex, $H_p B_q$, should be



$$K_{pq} = [H_p B_q]/b^p h^q$$

where b represents the free concentration $[VO_3^-]$.

The data $Z(\log h)_B$ were analyzed by means of the computer programs 1) Mesak,⁸ which calculates the average composition (\bar{p}, \bar{q}) of the complexes, and 2) Letagropvrid,⁴ which searches for the set

of complexes and equilibrium constants (p,q,K_{pq}) , that minimizes the error square sum $U = \sum (Z_{exp} - Z_{calc})^2$.

Assuming that for $Z = 0$ ($z = -1$), the species (0,3) and (0,4), predominate,³ Mesak indicated that in the range studied complexes exist with an average composition $\bar{p} \approx 3-5$ and $\bar{q} \approx 6-10$.

Table 1 brings together an extract of the calculations carried out by means of Letagropvrid. The equilibrium constants are given as $\log(K \pm 3\sigma)$ as discussed in Ref. 7. The equilibrium constants for (1,1), (3,5), (4,7), (4,8), (4,9), and (4,10) all came out negative at the minimum.

The second set of complexes, (0,3), (0,4), (3,6), (5,10), and (6,10), gave a good fit with the data, and even if some improvement (a lower $\sigma(Z)$) could be obtained by adding (2,1), (5,9), and (6,9), (giving 8 complexes altogether) we prefer the combination of the five complexes mentioned until there are data over a broader range. It is remarkable that our experiments give some evidence for hexavanadates in addition to the decavanadates well established by Rossotti and Rossotti.

Experimental details are given in a report in Spanish.⁵

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1. Rossotti, F. and Rossotti, H. *Acta Chem. Scand.* **10** (1956) 957.
2. Brito, F. and Ingri, N. *Anales Fis. Quim. (Madrid)* **B 56** (1960) 165; *Acta Chem. Scand.* **13** (1959) 1971.
3. Brito, F., Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **18** (1964) 1557.

4. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 173.
5. Brito, F. *Anales Fis. Quim. (Madrid)* **B 62** (1966) 123.
6. Sillén, L. G. *Acta Chem. Scand.* **15** (1961) 1981.
7. Dunsmore, H., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **17** (1963) 2644.
8. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.

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Gas Chromatographic Analysis of Lignin Oxidation Products. The Diphenyl Ether Linkage in Lignin

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In connection with studies on the behaviour of lignin in pulping, we intended to follow possible condensation reactions by examining the aromatic carboxylic acids formed on permanganate oxidation of the methylated lignins. This type of lignin degradation and the careful separation of the arising mixture of aromatic carboxylic acids by distribution between solvents, column chromatography, and crystallization has been reported by Freudenberg *et al.*^{1,2} For our purpose, it was desirable to replace this tedious combination of separation procedures by gas chromatographic analysis, which also could be expected to give more quantitative information.

In the work of Freudenberg *et al.*, the permanganate oxidation was carried out at pH 6–7. We found that considerably higher yields of the aromatic carboxylic acids were obtained if the oxidation was carried out at pH 12. However, the mixture of degradation products obtained at this pH value was found to contain appreciable amounts of phenylglyoxylic acids. These could be degraded to the corresponding aromatic carboxylic acids by subsequent

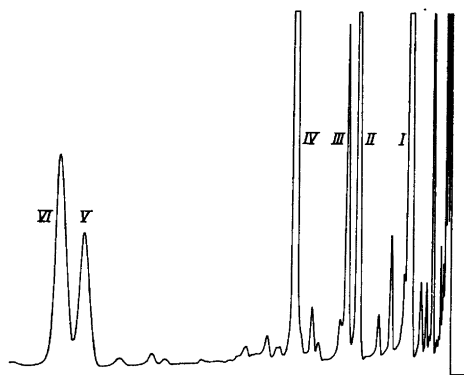


Fig. 1.

treatment with 5% H_2O_2 at pH 9–10. Finally, the mixture of carboxylic acids was methylated with diazomethane.

Gas chromatography of the mixture of methyl esters under the conditions given below effected good separation (Fig. 1). In Table 1, the amounts of the more prominent methyl esters obtained from diazomethane methylated Björkman lignin (spruce) as well as from Björkman lignin (spruce) pretreated in two different ways are given. The main products from the oxidative degradation thus are the methyl esters of veratric acid (I), isohemipinic acid (II), metahemipinic acid (III), 3',4,5-trimethoxy-3,4'-oxydibenzoic acid (V) and 5,5'-dehydro-diveratric acid (VI).

The tetramethyl ester of pyromellitic acid (IV) was added as internal standard for the quantitative determination. The significance of the relative amounts of

