Reactions of Ethyl Orthovanadate with Ethanolamines

By R. K. MITTAL

Summary

Reactions of mono-, di-, tri-ethanolamine and ethylene diamine with ethyl orthovanadate were carried out at different molar ratios, and the products were isolated. Tentative structures of the compounds are given.

Inhaltsübersicht

Es wurden die Produkte der Reaktionen von Triäthylorthovanadat, $VO(OEt)_3$, mit Mono-, Di-, Triäthanolamin und Äthylendiamin isoliert.

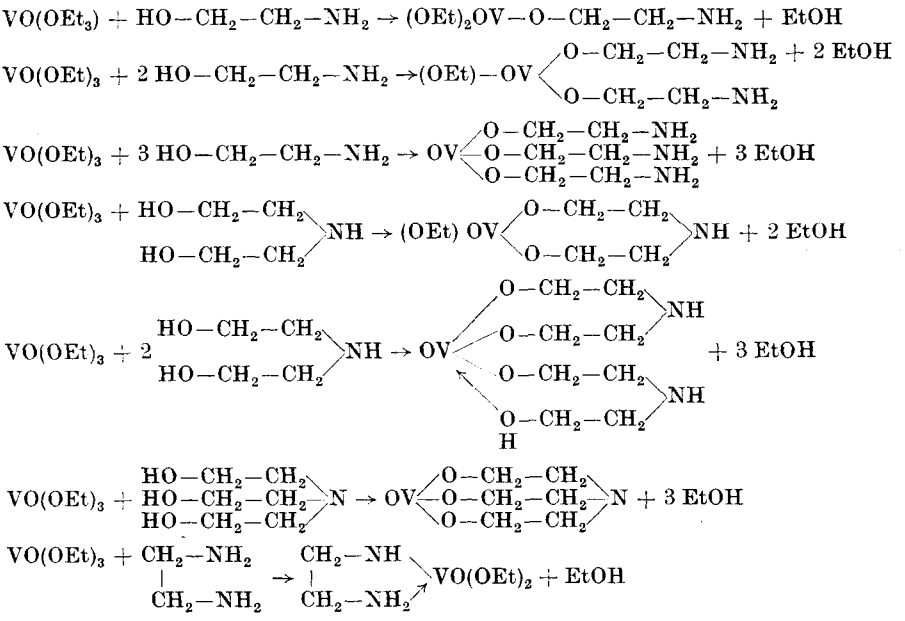
Reactions between ethanolamines and several metal alkoxides[1–6]) have been studied in these laboratories in recent years. In view of the interesting results obtained in these cases it was considered worthwhile to carry out these reactions with ethylorthovanadate also. A survey of the literature revealed that these reactions have not been studied with these alkoxides probably due to oxidising properties of pentavalent vanadium. The hydrogen of a hydroxyl group appears to take part in the replacement reactions in all the alkoxides studied so far with these ligands while the hydrogen of the amino group reacts only in some cases[4–6]). In the present investigations it has been observed that the hydrogen of the hydroxyl group takes part in the reaction. In order to confirm that the hydrogen of the amino group does not react with ethyl orthovanadate, reactions with butyl amine and di-n-butyl amine were also carried out and it has been found that even on refluxing for some time no substitution of alkoxy group takes place. However, one hydrogen of the ethylene diamine takes part in the replacement reactions.

The reactions were found to be facile and exothermic.

[1]) G. SRIVASTAVA and R. C. MEHROTRA, J. Indian chem. Soc. **39**, 521 (1962).
[2]) D. M. PURI and R. C. MEHROTRA, J. Indian chem. Soc. **39**, 447 (1962).
[3]) R. K. MEHROTRA and R. C. MEHROTRA, J. Indian chem. Soc. **39**, 677 (1962).
[4]) G. CHANDRA and R. C. MEHROTRA, Indian J. Chem. **3**, 497 (1965).
[5]) S. MATHUR and R. C. MEHROTRA, (Private communication).
[6]) V. D. GUPTA and R. C. MEHROTRA, (Private communication).

The products started separating from the reaction mixture soon after the reactants were added. The reaction mixture was thoroughly shaken for some time and then allowed to stand for an hour in order to ensure completion of the reaction. The compounds, yellow solids, were isolated by filteration in vacuum and were thoroughly washed with dry benzene. The compounds were dried by evaporating the solvent under reduced pressure at the room temperature. The identity of compounds was established by estimating vanadium (total as well as pentavalent vanadium separately) and nitrogen KJELDAHL's method).

The reactions can be represented by the following equations:



Experimental

All glass apparatus with standard interchangeable joints was used throughout this work, and special care was taken to exclude moisture.

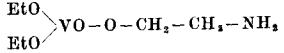
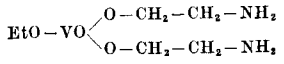
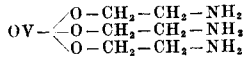
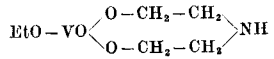
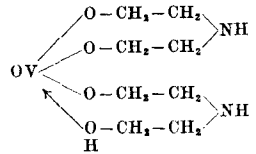
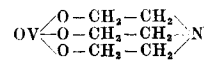
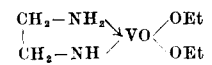
Material: Vanadyl triethoxide was prepared and solvents were dried as described in earlier communication[7]). The amino compounds were purified by distilling them before use.

Analytical methods: Vanadium as +5 state was ascertained volumetrically and total vanadium estimated gravimetrically as V_2O_5. Nitrogen content was determined by KJELDAHL's method.

Reaction of ethylorthovanadate with monoethanolamine in the molar ratio 1:1. When ethyl orthovanadate (3.322 g) was added to monoethanolamine (1.004 g) in benzene (5 g), sufficient heat was evolved and the colour of the solution became deep yellow. The separation of yellow solid immediately started which further increased on shaking. The reaction mixture was allowed to stand for about an hour in order to ensure completion of the reaction. The compound was then isolated by filtering and washing in the

[7]) R. K. MITTAL and R. C. MEHROTRA, Z. anorg. allg. Chem. **327**, 311 (1964).

Table 1
Reactions of ethyl orthovanadate and ethanolamines

Molar ratio	Ethylortho-vanadate g	Ethanolamine added g	Formula of the product	V^{+5} %	Total V %	Analysis Calc. %	N % found	Calc. %
Monoethanolamine								
1:1	3.322	1.01		23.40	23.45	23.50	6.40	6.46
1:2	3.390	2.05		22.0	22.03	22.0	12.20	12.1
1:3	3.540	3.270		20.60	20.74	20.64	16.85	17.0
Diethanolamine								
1:1	2,894	1.509		23.70	23.82	23.72	6.5	6.5
1:2	3.058	3.212		15.90	16.05	16.0	9,0	8.9
Triethanolamine								
1:1	3.638	2.70		23.81	23.94	23.94	6.45	6.5
Ethylenediamine								
1:1	2.96	0.87		23.60	23.70	23.60	12.94	13.0

vacuum. Benzene was stripped off under reduced pressure. The compound could not be distilled.

Found: V 23.40 (as +5); 23.45 (as V_2O_5); and N 6.4. Calc. for $(C_2H_5O)_2VOC_2H_6ON$: V 23.50, and N 6.46.

For brevity details of other reactions are listed in the Table 1. All reactions were carried out in benzene medium. They were found to be facile and exothermic. All prodcuts were separated from benzene. No noticeable reduction of pentavalent vanadium took place under these conditions. A reaction of ethylene-diamine was also carried out with ethyl orthovanadate.

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