

THE ACTION OF VANADIUM OXYTRICHLORIDE UPON VARIOUS ORGANIC COMPOUNDS

By R. E. NELSON and A. H. MCFADDEN, Purdue University

Since little work has appeared in literature concerning the action of vanadium oxytrichloride with organic compounds, and as it is known to be a very reactive substance, the study of its action on organic compounds should prove of interest.

Snyder and Brown . . . Snyder and Brown, *J. Am. Chem. Soc.*, **47**, 2671 (1925) . . . have studied vanadium oxytrichloride as a solvent. They stated that: "All of the purely organic compound either dissolved, reacted or both; the organic liquids were miscible in all proportions; the liquid aldehydes reacted vigorously; acetone is miscible and reactive as is also acetic anhydride." They do not state procedure details of the work.

Vernon . . . Vernon, *J. Am. Chem. Soc.* **53**, 3831 (1931) . . . has studied the action of vanadium oxytrichloride upon phenyl magnesium bromide.

Vanadium oxytrichloride, in this investigation, was allowed to react with several representative organic compounds to determine which compounds would be most likely to throw some light on the way in which vanadium oxytrichloride acts.

A summary of these preliminary reactions is given in Table 1.

TABLE I.

The Action of Vanadium Oxytrichloride with Various Organic Compounds.

Organic Compound	Action
1. Acetone	Black viscous precipitate
2. Benzaldehyde	Black grainy precipitate
3. Anhydrous benzene	Deep brownish red solution, no evidence of reaction
4. Anhydrous ether	Deep red solution. No evidence of reaction
5. Formaldehyde	White precipitate and intense blue solution
6. Acetophenone	Dark greenish blue solution
7. Acetaldehyde	Dark green solution
8. Quinoline	Green stable solid and quinoline hydrochloride
9. Benzene and anhydrous aluminum chloride	No evidence of reaction
10. Absolute alcohol	Brown solution with slight evolution of heat
11. 95 per cent alcohol	Yellow orange precipitate of vanadium pentoxide
12. Melted phenol	Reaction with evolution of hydrogen chloride
13. Potassium phthalimide	Reacted. One product isolated. Melted at 229° C.
14. Aniline	Black grainy solid
15. Monomethyl aniline	Black grainy solid
16. Dimethyl aniline	Black grainy solid

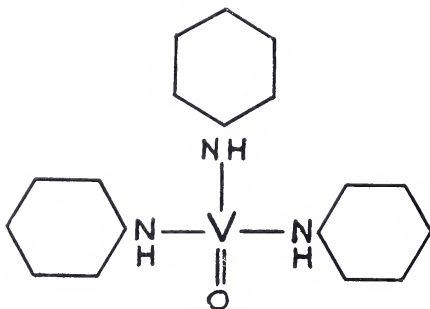
This work has been limited mainly to the study of the action of vanadium oxytrichloride with aniline and with benzaldehyde.

VANADIUM OXYTRICHLORIDE AND ANILINE

Vanadium oxytrichloride reacted with aniline to give a complexity of products, indicating that probably both a condensation and an oxidation had taken place. Aniline hydrochloride along with vanadium dioxide and vanadium tetraoxide have been isolated and identified.

A brownish red organic compound has been isolated and studied. This compound melts at 236° C. and was found to be soluble in ether, benzene, alcohol, concentrated sulphuric acid and concentrated nitric acid. An analysis showed the presence of nitrogen, carbon and hydrogen but no vanadium or chlorine. There was evidence of the presence of an azo group. An analysis for nitrogen by the Kjeldahl method gave 17 per cent. The compound was not identified.

The main product of the reaction, a black solid, was isolated and studied. Great difficulty was encountered in separating it from the oxides of vanadium. The fact that the substance was insoluble in any common reagents made it difficult to purify. Concentrated hydrochloric acid dissolved it and on neutralization with sodium hydroxide, aniline and oxides of vanadium were obtained. An analysis gave 12.5 per cent nitrogen and 16.54 per cent vanadium as compared to 12.24 per cent nitrogen and 14.86 per cent vanadium calculated for the following formula:



The high percentage of vanadium may be due to the difficulty of separating it from the oxides of vanadium.

This compound is a blue-black powder. It has no melting point; on heating it gradually becomes red hot and begins to glow as finely ground coal glows. It finally burns to an ash leaving vanadium pentoxide. On being treated with concentrated nitric acid (two drops on finely powdered solid) it bursts into flame.

VANADIUM OXYTRICHLORIDE AND BENZALDEHYDE

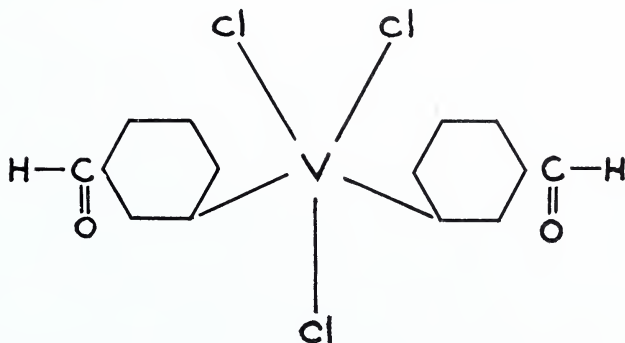
Vanadium oxytrichloride reacted with benzaldehyde to give a fine grainy black precipitate which was easy to filter and wash. This precipitate hydrolyzed on exposure to air, giving off hydrogen chloride and leaving an oily black residue. Benzoic acid and oxides of vanadium

were obtained from the mother liquors. The main product of this reaction proved very difficult to handle since even when in a vacuum desiccator it continued to give off hydrogen chloride gas. Attempts to run an accurate analysis was unsuccessful due to the rapid decomposition. Analysis made on the compound gave the following percentages:

	% Chlorine	% Vanadium
No. 1	23.9	13.4
No. 2	22.4	14.8
No. 3	20.4	14.9

This variation in the percentage of vanadium and chlorine can be accounted for by the fact that the decomposition of this compound caused the percentage of chlorine to drop and the percentage of vanadium to rise.

This product hydrolyzed with water to give benzaldehyde and vanadium pentoxide. A very probable formula for this condensation produce is:



Calculated 13.88 per cent vanadium, 29.0 per cent chlorine.

EXPERIMENTAL

The products of the different reactions were analyzed for vanadium, nitrogen and chlorine.

(a) Analysis for Vanadium.

Two-tenths to 0.5 g. of the sample was accurately weighed and ignited in a porcelain crucible, then cooled and three drops of concentrated nitric acid added to thoroughly oxidize the vanadium to V_2O_5 . The crucible was then steadily heated for about an hour to insure thorough ashing. It was weighed as vanadium pentoxide.

(b) Analysis for nitrogen was made by the Kjeldahl method.

(c) Analysis for Chlorine.

The sample was oxidized in a Parr bomb and then determined by the Volhard method.

THE ACTION OF VANADIUM OXYTRICHLORIDE UPON ANILINE

Twenty cc of vanadium oxychloride was added dropwise to 150 cc (an excess) of aniline dissolved in 200 cc of benzene. The mixture was stirred continuously. Considerable heat was generated. The reaction mixture was steam distilled to remove aniline and benzene. The black precipitate was filtered, dried and extracted in a Soxhlet extractor with benzene. It was dried again and then extracted with hot water to further purify it. The wash waters were found to contain aniline hydrochloride.

This blue black organic vanadium compound had no melting point but gradually became red hot and began to glow like finely granulated coal. On burning vanadium pentoxide remained. On treating the organic compound with concentrated nitric acid it bursts into flame. The analysis was as follows:

	Nitrogen	Vanadium
Calculated for $C_{15}H_{15}N_3VO$	12.24	14.86
Found	12.56	16.54

The benzene extract contained a red azo-like compound which was not identified.

Vanadium dioxide and vanadium tetroxide were formed in the reaction and the difficulty of separating these probably accounts for the high value in the analysis for vanadium.

THE ACTION OF VANADIUM OXYTRICHLORIDE UPON BENZALDEHYDE

Ten cc (1 mol) of vanadium oxytrichloride was run, as in the aniline experiment, in to an excess (3 mols) of benzaldehyde in benzene solution. The reaction mixture was stirred an hour, then the precipitate was filtered, washed with ether and put into a vacuum dessicator to dry. Hydrogen chloride was slowly evolved in the dessicator and copiously given off when samples were dried outside the dessicator. The residue after the loss of HCl was a black oily residue. Benzoic acid and oxides of vanadium were obtained from the mother liquors.

Attempts to run an accurate analysis were unsuccessful owing to the rapid hydrolysis.

Analysis	% Chlorine	% Vanadium
Calculated for $C_{11}H_{10}Cl_3VO_2$	29.0	13.9
Found	23.9	13.4
	22.4	14.8
	20.4	14.9

The product hydrolyzed with water to give benzaldehyde and vanadium pentoxide.

SUMMARY

1. The reaction between vanadium oxytrichloride and aniline has been studied.
2. The reaction between vanadium oxytrichloride and benzaldehyde has been studied.
3. The reaction of vanadium oxytrichloride with fourteen other organic compounds has been observed.