VANADIUM 8-HYDROXYQUINOLATE AS A REAGENT FOR THE DETECTION OF ALCOHOLS, THIOLS AND AMINES

by

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The black complex of 8-hydroxyquinoline with vanadate ("vanadium 8-hydroxyquinolate", $(C_9H_6ON)_2VO.OH)$ is known¹ to be slightly soluble in pure benzene and chloroform to give almost black solutions, but in commercial chloroform a bright red solution results. The difference has been ascribed² to the presence of alcohol in the commercial chloroform, and the colour change has been employed, in aqueous media, as a qualitative test for alcohols³. A mechanism for the reaction has been proposed, and the pure chloroform solution used as a test for some alcohols by BIELIG AND BAYER⁴. The present paper examines the reactions of most types of alcohols, and, indeed, of most classes of organic compounds, with vanadium 8-hydroxyquinolate and extends its usefulness as an organic analytical reagent. The authors propose to publish separately further observations on the mechanisms of the reactions involved.

The complex was found to be more soluble in tetrachloro-ethane and o-dichlorobenzene (solutions up to 1% have been prepared) than in chloroform, giving solutions that were shown by chromatography on alumina to contain one species only, but only sparingly soluble in trichloroethylene, tetrachloroethylene and pentachloroethane. The action of heat on a commercial tetrachloroethane solution leads to the formation of a blue colour that is known⁴ to be due to the formation of an inner-complex salt of the formula $[(C_9H_6ON)_2.V(OH)_2]Cl$ with the hydrogen chloride that arises from hydrolysis of the solvent by small quantities of moisture that are normally present. A rigourously dried solvent does not cause this colour change, unless the reagent solution is exposed to light for a long period, when the photochemically produced hydrogen chloride again forms the blue solution. Similar reactions with organic compounds are obtained with the black and blue forms, but the blue variety was found to be less sensitive than the black.

ENPERIMENTAL

Reagents

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^{1.} Vanadium 8-hydroxyquinolate⁵. To a hot, weakly acid solution of ammonium vanadate, buffered with ammonium acetate (pit 3 to 6), add a 2% solution of AR 8-hydroxyquinoline in 5% acetic acid until precipitation is complete. Collect the black precipitate on a sintered-glass filter, wash with hot water and dry at 120° C. Purify by boiling the finely crushed product with benzene to remove co-precipitated 8-hydroxyquinoline, filter, wash with hot benzene and dry at 120° C. 2. Tetrachloroethane. Dry B.D.H. technical tetrachloroethane over freshly ignited lime.

3. o-Dichlorobenzene. Distil B.D.H. technical o-dichlorobenzene. Reject the first 5% and collect the fraction of boiling point 180-182° C. (By means of the reagent the presence of alcoholic hydroxyl groups may be demonstrated in some specimens of technical o-dichlorobenzene).

4. Reagent solution. Dissolve 18-19 mg of vanadium 8-hydroxyquinolate in 250 ml of dry tetrachloroethane by warming to 70-80° C. The resulting solution is approximately $2 \cdot 10^{-4} M$.

The reagent solution may also be prepared rapidly and directly from ammonium vanadate and 8-hydroxyquinoline as follows: dissolve 50 mg of AR 8-hydroxyquinoline in 100 ml of tetrachloroethane or o-dichlorobenzene, and add approximately 50 mg of AR ammonium vanadate. Maintain the mixture at 130° C for half an hour, cool and filter. Dilute, if necessary, to give a solution of the same colour intensity as the reagent prepared from the solid. The reagent prepared in this way is not so sensitive to small quantities of alcohols because the excess of 8-hydroxyquinoline inhibits the colour change from black to red.

Reactions of the tetrachloroethane solution

Procedure. To 1-2 ml of the reagent solution add 2-3 drops, or about 0.1 g of the compound to be tested, (this corresponds to a molecular ratio of 5000 : 1 for a molecular weight of 100). If no colour change occurs in 10-15 minutes, warm gently and examine the solution after it has cooled to room temperature.

The following table summarizes the results obtained:

COMPOUND

REACTION

1. Simple alcohols Methanol^{3,4}, ethanol^{3,4}, iso-propanol^{3,4}, n-3, Black to permanent red in the cold. The tertalcohols react much more slowly than the others. sec-, tert-butanol, n-pentanol³, decyl alcohol, (The colour with benzyl alcohol slowly fades tri-n-amyl carbinol, cetyl alcohol, 2 : 4-dihydroxy-2-methyl pentane, 2-hydroxyethyl meto yellow.) thyl ether, glycerine³, diacetone alcohol³, allyl alcohol, cyclohexanol³, benzyl alcohol. 2. Other alcohols Pentaerythritol, triphenyl carbinol. Black to dark purple on warming. No change. Higher polyhydric alcohols (mannitol, sorbitol), simple sugars and sugars with two or three blocked hydroxyl groups. 3. Thiols Black to bright green in the cold. Turned lemon-Ethyl, benzyl, p-nitrobenzyl and lert-butyl mercaptans. yellow by a large excess. (Except lert-butyl.) Thiophenol. Black to green to deep yellow in the cold. 4. Amines (a) Aliphatic. n-butylamine, tetradecylamine. Black to light golden yellow in the cold. Triethylamine. Black to light green in the cold. (b) Aromatic. Aniline. Black to dark green in the cold. No rapid change, hot or cold, black to deep Methyl aniline. orange-yellow overnight. No rapid change, hot or cold, black to dark Dimethyl aniline. green in two days. Black to yellow on warming. Pyridine. Diphenylamine. No change. 5. Peroxides Dibenzoyl peroxide. No change.

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	tert-butyl hydroperoxide. tert-butyl hydroperoxide + ethanol.	Grey emulsion in the cold, going brown in an hour and finally yellow. On heating, grey to yellow via a fleeting red. Black to red (normal alcohol reaction), then fading to yellow in two hours.
6.	Carboxylic acids and phenols	
	Acetic acid ⁴ , phenol ³ , phloroglucinol. Trichloroacetic acid. Caproic, stearic and mucic acids. Thioacetic acid (CH ₃ .CO.SII).	Black to blue in the cold. Immediate black to blue, green with excess. No change. Black to blue to dark green to light green in the cold.
7 .	Polyfunctional compounds	
	2-Mercaptoethanol. Diethylethanolamine, ethanolamine.	Black to orange-yellow in the cold. Black to red instantaneously, soon fading to yellow.
	Amino-acids.	No change.
	Thio-urea. Phenyl thio-urea	Black to dark green on warming.
	1:3-Dimercapto-2-hydroxypropane. 1:2-Dimercapto-3-hydroxypropane.	Black to green to yellow in the cold. Black to red to yellow-brown in the cold, slowly fading to yellow.
	Thioglycollic acid.	Decolorized in the cold.
8.	Keto-Enol tautomers	
	Diethyl malonate, ethyl acetoacetate, 1:4:4- tricarbethoxy-1-en-3-one.	No change. (Commercial acetoacetic ester con- tains ethanoland gives the usual alcohol reaction).
9.	Miscellaneous compounds	
	Dicyclohexylidene glucose.	Black to dark purple on warming.
	DL-Penicillamine hydrochloride,	Black to blue in the cold,
	Activit ester or the above,	ing.
	N-(3:4:6-triacetyl D-glucosyl)-piperidene, 2-phenyl-3-thio-4:6-dimethyl-5-keto-a-triazine. 2-Thio-4-carbethoxy-5:5-dimethyl-thiazolidine.	Black to yellow on warming. (The former prob- ably partially decomposes to piperidene.) No change.
	Dimethylglyoxime. Diphenylcarbazide.	Black to brownish-yellow on warming. Black to yellow-brown in the cold; becoming deep crimson on standing.

DETECTION OF ALCOHOLS, THIOLS AND AMINES

10. The following classes of compounds do not react with the reagent:

Hydrocarbons, halogenohydrocarbons, aldehydes, ketones, ethers, amino-acids, nitro-compounds, nitriles, esters and simple sugars.

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Conclusion. Vanadium S-hydroxyquinolate is a specific reagent for the detection of alcohols, a colour change from black to red in the cold being a positive reaction. Only those alcohols which are completely insoluble in tetrachloroethane (e.g. mannitol and simple sugars) do not react. The reagent is not completely specific for amines; the majority give a golden yellow colour, but some react very slowly and others not at all. All thiols react in a fairly uniform manner, but some amines react to give a golden yellow colour which is not easily distinguishable from the lemon yellow produced by thiols. The o-dichlorobenzene solution may be used as a reagent for acidic substances: a colour change from black to blue is caused by low molecular-weight carboxylic acids, phenols and all hydrochlorides⁴. (If any substance which is not dry is added to the reagent in *tetrachloroethane* and the solution warmed, the black colour changes to blue.)

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Notes: (i) The mixture should not be heated strongly when testing for alcohols, as the red colour of the solution fades at high temperatures. However, in nearly all instances, except in those of some cyclic alcohols, the colour returns on cooling.

(ii) Most compounds that do not react with the reagent, do not interfere with the alcohol reaction, but phenols (including 8-hydroxyquinoline) and low molecular-weight carboxylic acids inhibit the colour change from black to red when only small amounts of the alcohol are present.

(iii) The tetrachloroethane used in making up the reagent solution must be dry, if the damp solvent is used, the solution may become blue on long standing. The blue solution gives the same reactions as the black solution, but is less sensitive to small amounts of alcohols, since the colour change is inhibited by acids.

(iv) Similar results are obtained by using a tetrachloroethane solution of the green anhydride of vanadium 8-hydroxyquinolate, $(C_0H_6ON)_2 = VO-O-VO = (C_0H_6ON)_2$, which is prepared by heating the black complex at 250° C for 30 minutes or by the prolonged boiling of its solution in tetrachloroethane under a dry atmosphere. However, the green solution is not recommended as a reagent as it is not possible to detect small quantities of thiols or amines with it.

(v) *o*-Dichlorobenzene is an excellent solvent for vanadium 8-hydroxyquinolate and may be used in place of tetrachloroethane for preparing the reagent solution. The complex dissolves readily on warming to give a black solution and the colour does not change to blue on heating, even if the solvent is moist, because *o*-dichlorobenzene is not readily hydrolyzed. On heating the solution to boiling (180° C) , the colour fades to a light yellow and returns to black on cooling. This black solution gives the same reactions as the tetrachloroethane solution in nearly all instances, except that it is not turned blue by acids so readily.

Detection of ethyl alcohol in aqueous media

If the reagent is shaken with aqueous alcohol, the usual colour change from black to red occurs, the time required for a visible change depending on the alcohol concentration. The following reactions were obtained on typical aqueous solutions:

Wine. On shaking the reagent with an equal volume of wine, the black colour changed to red almost immediately. (No red colour is extracted from wine by pure tetrachloroethane.)

Beer. The emulsion formed on shaking the reagent with beer takes a long time to separate into two distinct layers; the black colour of the reagent layer had changed to a dark purple in two hours and to red on standing overnight. No colour is extracted from beer by pure tetrachloroethane.

Blood. If blood was shaken with the reagent a red emulsion resulted and no colour change could be observed. The blood was centrifuged to remove the red corpuscles, and the clear liquid shaken with an equal volume of reagent solution of half the usual concentration. Blood containing 1% of alcohol gave a tositive test in three hours, whereas normal blood gave no reaction on standing in contact with the reagent overnight.

Sensitivity of the alcohol-detection reaction

It was found that a ratio of 50 molecules of a primary alcohol, 100 molecules of a secondary alcohol or 500 molecules of a tertiary alcohol to one molecule of vanadium 8-hydroxy-quinolate gave a positive reaction in 10-15 minutes.

The minimum satisfactory concentration for the reagent solution is $10^{-4}M$. In a micro-centrifuge-cone, the colour change may be seen with 0.1 ml of reagent + 0.1 ml of test solution. With a molecular ratio of 50 : 1, this corresponds to approximately 20 μ g of ethanol in 0.1 ml. Dilution limit: 1 in 5000.

Similarly for the butanols, the limits are:

40 μ g *n*-butanol at a dilution limit of r in 2500,

So μg of sec-butanol at a dilution limit of r in 1250, and

400 μ g of *tert*-butanol at a dilution limit of I in 250.

If the alcohol is left in contact with the reagent for 24 hours, a positive reaction is obtained with a molecular ratio of 12:1, 25:1 and 125:1 for primary, secondary and tertiary alcohols respectively.

Light-absorption curves

Light-absorption curves, measured in 1 cm cells with a Uvispek Spectrophotometer, are given for solutions of vanadium 8-hydroxyquinolate in tetrachloroethane (Fig. 1): (a) Black solution in anhydrous solvent.

- (b) Blue solution obtained by heating in moist solvent.
- (c) Red solution obtained by addition of an excess of ethanol.
- (d) Yellow solution obtained by addition of an excess of ethyl mercaptan.
- (e) Yellow solution obtained by addition of an excess of n-butylamine.
- all of which contained 7.3 mg of vanadium 8-hydroxyquinolate in 100 ml.



Fig. 1. Absorption curves of vanadium 8-hydroxyquinolate in tetrachloroethane.

A. Black solution in anhydrous solvent.

B Blue solution obtained by heating in moist solvent.

C. Red solution obtained by addition of an excess of ethanol.

D. Yellow solution obtained by addition of an excess of ethyl mercaptan.

E. Yellow solution obtained by addition of an excess of butylamine.

All these solutions contained 7.3 mg of vanadium 8-hydroxyquinolate per 100 ml.

Conversion of vanadium 8-hydroxyquinolate to the red form with increasing quantities of various alcohols

It is seen from the absorption-curves that the red form has virtually no absorption above 7000 A, while the black form absorbs up to 10000 A. If the optical density is measured at 7000 A, the progress of the reaction may be followed.

Batches of solutions, all containing the same concentration of vanadium 8-hydroxyquinolate, and containing increasing molecular ratios of ethyl, cetyl, *n*-butyl, *sec*-butyl *References p.* 7 and *tert*-butyl alcohols were prepared. The optical density of each member of each batch was measured at 7000 A in a 1 cm cell with a Unicam S.P. 600 Spectrophotometer; and curves were plotted of optical density against the molecular ratio of the alcohol to the complex. Fig. 2 shows the curves obtained when the solutions had reached equilibrium, (after about a week). Smooth curves were obtained in all instances, whether equilibrium had been reached or not, provided that measurements on all members of a batch were made at the same times after mixing the reagents.

By comparison with a set of standards, the reagent may be used for the semi-quantitative determination of alcohols, in the absence of interfering substances. For quantitative use, the greatest accuracy is obtained if quantities are chosen to give a molecular ratio of between 10 and 50 of the alcohol to one of vanadium 8-hydroxyquinolate (for

p-and sec-alcohols). It must be stressed that the standards must be treated under conditions identical to those of the test solutions, as the intensity, which appears to be dependent on an equilibrium between the black and the red forms, is sensitive to temperature.

Fig. 2. Curves showing the relation between optical-density at 7000 A and molecular ratio of alcohol to vanadium 8-hydroxyquinolate in tetrachloroethane; the solutions having reached equilibrium. A. *tert*-butyl alcohol, B. *n*-butyl alcohol. Curves almost identical with B. were given by ethyl, *sec*-butyl and cetyl alcohols.



Relative effect of active groups on the reagent, and interconversion of the reaction products **1**. Alcohols and mercaptans

(a) Addition of a large excess of ethyl mercaptan to a solution turned red by approximately 100 molecular equivalents of ethyl alcohol caused a slow change from red through orange to yellow.

(b) Upon addition of a large excess of ethyl alcohol to a solution turned greenishyellow by a small quantity of ethyl mercaptan, the colour slowly deepened through orange to red.

2. Alcohols and amines

(a) Addition of a drop of *iso*-propylamine to a red solution containing a large excess of ethyl alcohol caused a fairly rapid fading of the colour through orange to yellow.

(b) Addition of a very large excess of ethyl alcohol to a yellow solution containing a trace of *iso*-propylamine produced no immediate effect, the solution became orangered on standing overnight.

3. Alcohols and acids

The blue form of vanadium 8-hydroxyquinolate is less sensitive to small quantities of alcohols than the black form. Addition of acids (the lower carboxylic acids or phenols) to a red solution caused a partial reconversion to the blue form when only small quantities of alcohol were present.

4. Mercaptans and acids

On addition of ethyl mercaptan to a solution of vanadium 8-hydroxyquinolate in tetrachloroethane turned blue by acetic acid, the colour changed to green or yellow depending on the quantity of mercaptan. Addition of much acetic acid to the green or yellow solution produced no colour change, but formic acid caused the colour to revert to blue.

5. Acceleration of the reaction with alcohols by bases

That the colour change from black to red with alcohols is accelerated by bases is shown by the fact that ethanolamine reacts much more quickly than ethanol and by the following experiment: 2 drops of ethanol were added to I ml of the reagent, followed by a drop of *n*-butylamine. The colour immediately changed from black to orange-red and slowly faded to yellow; a blank, containing the same quantities of alcohol and the reagent took a few minutes to become red.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Imperial Chemical Industries, Ltd. for a maintenance grant to A.J.B.

SUMMARY

The 8-hydroxyquinolate of pentavalent vanadium ("vanadium 8-hydroxyquinolate", $(C_0H_0ON)_2$, VO.OH) dissolves in a number of chlorohydrocarbons to give deep blue-black solutions. These solutions undergo distinctive colour changes upon addition of acids (blue), alcohols (red via purple), thiols (yellow via green) and amines (yellow via green), provided that these reagents are soluble in the chlorohydrocarbon. These sensitive and specific qualitative tests are extended to the semiquantitative determination of alcohols. For comparable compounds the rate of reaction with vanadium 8-hydroxyquinolate is as follows: $[-NH_2 = NH, \pm N] > [-CH_2OH, -CH_2SH] > [=CHOH, =CHSH] > [= COH, = CSH].$

RÉSUMÉ

Le 8-hydroxyquinoléate de vanadium (V), $(C_9H_6ON)_9$ VO.OH, est soluble dans un certain nombre d'hydrocarbures chlorés en donnant des solutions bleu noir. Ces solutions changent de couleur par addition d'acides (bleu), d'alcool (rouge, en passant par pourpre), de thiols (jaune, en passant par vert), d'amines (jaune, en passant par vert), à condition que ces réactifs soient solubles dans l'hydrocarbure chloré. Cos réactions qualitatives, sensibles et spécifiques, peuvent être utilisées pour le dosage semiquantitatif des alcools. La nature des substituants influence la vitesse de réaction avec l'hydroxyquinoléate de vanadium. Pour des composés analogues, cette vitesse de réaction varie dans l'ordre suivant: $[-NH_2, =NH, \equiv N] > [-CH_2OH, -CH_2SH] > [=CHOH, =CHSH]$ > [\equiv COH, \equiv CSH].

ZUSAMMENFASSUNG

Das 8-Hydroxychinoleat von Vanadium (V) (C_9H_6ON)₂VO.OH, ist in einer gewissen Anzahl von Chlorkohlenwasserstoffen löslich und gibt schwarz blaue Lösungen. Diese Lösungen ändernihre Farbe durch Zugabe von Säure (blau), von Alkohol (geht es über purpur zu rot), von Thiol (über grünzu gelb) von Aminen (über grün zu gelb) unter der Bedingung dass diese Reaktive in Chlorkohlenwasserstoff löslich sind. Diese qualitativen Reaktionen, empfindlich und speziefisch, können für semiquantitative Alkoholbestimmungen verwendet werden. Die Art der Substituenten beeinflusst die Reaktions-Geschwindigkeit mit Vanadium-hydroxychinolein. Für analoge Verbindungen variiert diese Reaktions-Geschwindigkeit in folgender Ordnung: $[-NH_2, =NH, \equiv N] > [-CH_2OH,$ $-CH_{s}SH$ > [=CHOH, =CHSH] > [=COH, =CSII].

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Received December 16th, 1954