# The Iodometric Determination of Propargyl Alcohol

By Kazumi YAMAMOTO, Minoru YOSHIMURA and Manzo TANAKA

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## Introduction

Our studies were conducted to estimate the quantities of propargyl alcohol in the reaction products which are formed by the reaction of formaldehyde and acetylene in accordance with the so-called "Reppe's alkynol synthesis".

As propargyl alcohol has the active methyne group, some of the well known analytical methods for the acetylenic compounds were employed. They did not give any satisfactory results, presumably either for the reason of the method itself being imperfect or by the interfering action of formaldehyde which usually remains in the product.

Our new method gave good results, especially, in the presence of formaldehyde too.

**The Outline of the Several Methods Already Known:**—(A) Argentometry of propargyl alcohol is not suitable in the case when formaldehyde is present as indicated by Hanna and Sigga.(1)

(B) The methods(2,3) in which propargyl alcohol is precipitated as Cu-compound and then determined indirectly, are also not suitable, because the Cu-compound of propargyl alcohol precipitated with Ilosvay's reagent(4) is not merely $Cu-C\equiv C-CH_2OH$ but the mixture with $Cu(C\equiv C-CH_2OH)_2$, in proportion to the quantities of the reagent added.

(C) Potassium mercuric iodide method.(1) This method was recently proposed by Hanna and Sigga and gave good result for pure propargyl alcohol. The determination of propargyl alcohol is based on the following reaction.

$$2CH\equiv C-CH_2OH+K_2HgI_4+2NaOH$$
$$=(OH-CH_2-C\equiv C)_2Hg+2KI+2NaI+2H_2O$$

We have observed, however, that this method is not applicable too, in the presence of formaldehyde of more than 0.5 %.

According to our experiments, the reaction between formaldehyde and potassium mercuric iodide is expressed as follows:—

$$K_2HgI_4+CH_2O+3NaOH$$
$$=2KI+HCOONa+Hg+2H_2O+2NaI$$

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(1) Hanna and Sigga, *Anal. Chem.*, **21**, 1469 (1949).
(2) Hein and Meyer, *Z. Anal. Chem.*, **72**, 30 (1927).
(3) Willstätter, *Ber.*, **53**, 936 (1920).
(4) Ilosvay, *Ber.*, **32**, 2697 (1910).

In case both propargyl alcohol and formaldehyde are present, however, the stoichiometric relation between formaldehyde and potassium mercuric iodide indicates considerable deviation.

## Our New Method

We observed that one mole of propargyl alcohol reacts with one mole of iodine quantitatively in alkaline solution and this reaction proceeds as follows:—

$$HC{\equiv}C-CH_2OH+I_2+NaOH$$
$$= IC{\equiv}C-CH_2OH^{(5)}+NaI+H_2O$$

So, the excess of iodine may be backtitrated with standard thiosulfate solution after acidification. The result obtained has agreed well with the one by Hanna's method as shown in the following tables.

If the sample contains formaldehyde, which also reacts with iodine quantitatively as already known, the quantity of propargyl alcohol can be calculated by subtracting the amount of iodine corresponding to formaldehyde from the total of iodine consumed. The former is calculated from the quantity of hydrochloric acid determined in oximmetry of formaldehyde in another run of the same sample.

$$CH_2O+NH_2OH\text{-}HCl=CH_2NOH+H_2O+\underline{HCl}$$
$$CH_2O+I_2+3NaOH=HCOONa+2NaI+H_2O$$

**Reagents to be used:—**

*ca.* 1*N* Sodium hydroxide solution,
*ca.* 1*N* Sulfuric acid solution,
*ca.* *N*/10 Iodine solution,
*N*/10 Sodium thiosulfate solution,
*ca.* *N*/10 Hydroxylamine hydrochloride solution,
*N*/10 Sodium hydroxide solution

**Indicators:**—Starch solution, Methyl orange.

**Procedure of analysis:**—The sample containing 0.02 to 0.06 g. of propargyl alcohol is accurately taken and diluted to 10 cc. with water in conical beaker of 300 cc. capacity, then pipetted in by shaking 25 cc. of *N* NaOH solution and 25 cc. of *N*/10 iodine.

After letting it stand for about 10 minutes, 35 cc. of *N* sulfuric acid is added, thus liberated excessive iodine is titrated with *N*/10 sodium thiosulfate as usual. Let us assume the volume of thiosulfate required as *a* cc.

Separately, blank run is held. Let us assume the volume of thiosulfate required in the blank run as *b* cc.

So the quantity of propargyl alcohol (P.A.) is calculated as follows:—

$$\text{P. A.}=0.005606\ \text{g.}\times\frac{b-a}{2}. \qquad (1)$$

In case when formaldehyde is present, first, $(b-a)$ cc. of thiosulfate is determined as above. Using the same sample the quantity of formaldehyde is separately determined with hydroxylamine hydrochloride as usual.

Let us, then, assume the volume of *N*/10 sodium hydroxide required for neutralizing hydrochloric acid liberated, as *c* cc. So the quantity of propargyl alcohol is calculated as follows:—

$$\text{P. A.}=0.005606\ \text{g.}\times\frac{(b-a)-2c}{2} \qquad (2)$$

The results obtained are shown in Tables 1 and 2.

Table 1

Result of Analysis of Pure Propargyl Alcohol

| P. A. weighed, | Our method calculated by Eq. (1), | Hanna's method, |
|---|---|---|
| g. | g. | g. |
| 0.1018 | 0.1016 | 0.1014 |
| 0.05070 | 0.0506 | 0.05063 |
| 0.01018 | 0.01015 | 0.01014 |

Table 2

Result of Analysis of P. A. Containing $CH_2O$

| Sample weighed | | $CH_2O$ by oximmetry | P. A. calculated by Eq. (2), |
|---|---|---|---|
| | g. | g. | g. |
| P. A. | 0.06198 | | 0.06199 |
| $CH_2O$* | 0.0018 | 0.0018 | |
| P. A. | 0.06198 | | 0.06196 |
| $CH_2O$* | 0.0180 | 0.0180 | |
| P. A. | 0.06198 | | 0.06200 |
| $CH_2O$* | 0.1703 | 0.1702 | |

* These values are determined by usual iodometry.
P.A. and $CH_2O$ were weighed separately and mixed before determination.

We have applied this method to the determination of methyl-(2)-butyne-(3)-ol-(2) which is prepared from acetylene and acetone, as well.

The result obtained was as follows:—

| Sample taken | Our method | Hanna's method |
|---|---|---|
| 0.05312 g. | 0.05310 g. | 0.05299 g. |

**Remarks:**—Our method indicates some deviation in result if the amount of formaldehyde exceeds three times of the amount of propargyl alcohol.

The effect of butyne-(2)-diol-(1.4) on the result is negligible. If the concentration of the sample and reagents are too high or the temperature is much higher than room temperature, the

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(5) We synthesized this compound in the same reaction and identified.

result obtained often indicates high value which is due to the formation of 3, 3, 2-triiodo allyl alcohol.

$$\mathrm{HO\text{-}CH_2C{\equiv}CH+2I_2+NaOH = HOCH_2CI{=}CI_2+NaI+H_2O}$$

This method suggests that it can be applied to the determination of the acetylenic derivatives of type of $\mathrm{RC{\equiv}CH}$.

## Conclusions

(1) It is impossible to determine propargyl alcohol in the reaction products which are formed by the reaction of acetylene and formaldehyde, by the already known methods.

(2) In order to determine propargyl alcohol under such conditions we invented new analytical method which is based on iodometry of propargyl alcohol.

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*Research Laboratory of*
*the Miike Dyestuff and Chemical Works,*
*Mitsui Chemical Industry Co., Ltd.,*
*Omuta, Fukuoka*