Determination of Ethylene

By

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Introduction

The determination of ethylene in the synthetic gas or waste gas is very important in petrochemical industry. Bromine solutions and fuming sulfuric acid adopted as usual are unsatisfactory for the determination of ethylene because the rates of absorption by them are slow and they attack paraffines.[1) 2)] Concentrated sulfuric acid activated 0.6% silver sulfate is unsatisfactory for the same reason.[1)] A solution of 3.5% silver sulfate in 72% sulfuric acid[3)] has been found to be unreliable because the absorption of ethylene in it is reversible. In fact, a sample of air desorbs ethylene from the reagent and increases in volume. A. W. Francis reports[4)] that 22% mercuric sulfate in 22% sulfuric acid is more satisfactory for that purpose because his proposed reagent does not attack paraffines, it absorbs ethylene irreversibly and it does not absorbs carbon monoxide or hydrogen. However, the absorption rate of ethylene by this reagent is not so fast. The absorption of ethylene by the aqueous solution of silver nitrate has been already studied by many researchers,[5) 6)] but a satisfactory reagent could not be obtained on account of the reversibility of absorption of ethylene. In order to find out the most satisfactory reagent, the mixed solutions of silver nitrate and salt or acid soluble in water were investigated. It was found that the mixed solution of silver nitrate and mercuric acetate was the most satisfactory.

Experimental and Discussion

1. Decision of Absorbent of Ethylene

Samples of 50cc were analyzed in a conventional Orsat apparatus. A sample was passed through the reagent (200cc) untill the absorption was complete or untill a constant reading was attained. The time of one pass was 14—18 sec. Investigating the solutions which absorb ethylene rapidly, a mixture of 5% silver nitrate solution 100 cc and added solution 100 cc was satisfactorily obtained. Next, the solutions which absorb ethylene irreversibly had to be found out. For that purpose, a 50 cc sample of air was passed ten times through each solution after a 4o cc of ethylene was absorbed.

A part of these results was shown in Table 1.

Table 1.

Added solution 100 cc	H_2O	EtOH	AcOH	89% H_3PO_4	95% HNO_3	1% Ni_2SO_4	5% $Hg(NO_3)$	5% $Hg(OAc)_2$
Volume after passes of air cc	52.3	54.6	54.0	65.0	54.2	56.4	50.0	50.0

In the case of the last two salts (mercuric nitrate and mercuric acetate), the sample of air returned unchanged in volume, indicating no reversible absorption. It is reported[4)] that mercuric nitrate which require nitric acid to prevent hydrolysis may become explosive when continued with large amounts of olefines. Therefore, mercuric acetate which forms a 25% solution in water without hydrolysis is more satisfactory. A gas mixture containing 20 cc of ethylene and 30 cc of air was passed through the reagent (a solution of 2.5 % silver nitrate and 2.5 % mercuric acetate) and only five passes were required for complete absorption. With bromine solution or concentrated sulfuric acid activated 0.6 % silver sulfate, over ten passes were required. Sample of pure hydrogene and isobutane were analyzed with this solution of silver nitrate and mercuric acetate. A sample of 50 cc showed no change in volume on passing into this solution ten times. A sample of carbon monoxide was not passed, but similar result may be obtained. A fresh sample of propylene was similarily absorbed and a sample of isobutylene was also slowly absorbed. These higher olefines and carbon dioxide should be first removed. As it is reported[7] that the addition of hydrochloric acid liberates propylene from the mercuric acetate-propylene complex, this reagent which absorbed a large amount of ethylene may be recovered by the similar procedure.

2. Absorption Rate of Ethylene

The absorption rate of ethylene was not affected by varying the concentration of mercuric acetate at a constant concentration of silver nitrate, but extremely increased by increasing the concentration of silver nitrate at a constant concentration of mercuric acetate. The concentration of silver nitrate governs the absorption rate of ethylene. The correlation between the absorption of ethylene (50 cc) and the concentration of silver nitrate at a definite concentration (0.4 %) of mercuric acetate was given in Table 2.

Table 2.

0.4 % $Hg(OAc)_2$

passes / concn. of $AgNO_3$ %	Volume of C_2H_4 cc 0	1	2	3	4	5	6	7	8
0.85	50.0	43.5	38.2	33.0	29.2	26.1	22.2	20.0	19.0
1.7	50.0	38.4	28.5	21.2	17.3	13.2	12.0	10.5	9.0
3.4	50.0	34.1	24.2	16.0	10.5	8.0	6.5	6.0	
6.8	50.0	18.5	8.2	6.3	5.5				

3. Maximum Saturated Absorption of Ethylene

By adding mercuric acetate, the reversibility of absorption of ethylene could be prevented. The correlation between this reversibility and the concentration of mercuric acetate was investigated. The reagents varying the concentration of mercuric acetate were prepared at a definite concentration (1.7 %) of silver nitrate.

A sample of 50 cc of ethylene was passed into each reagent and a sample of 50 cc of air was also passed. Unless a sample of air desorbs ethylene from the reagent and increases in volume, a sample of 50 cc of ethylene was again passed into the reagent. This procedure was repeated untill a sample of air desorbs ethylene and increases in volume.

Table 3.

1.7 % $AgNO_3$

Concn. of $Hg(OAc)_2$ %	0.4	0.8	1.6	3.2
Volume of max. absorption cc	59.0	90.2	190.5	406.0

0.4 % $Hg(OAc)_2$

Concn. of $AgNO_3$ %	0.8	1.7	3.4	6.8
Volume of max. absorption cc	54.5	59.0	63.1	72.0

The total volume of absorbed ethylene or the volume of maximum saturated absorption of ethylene against the concentration of mercuric acetate was shown in Table 3.

In the same Table, the results varying the concentration of silver nitrate at a definite concentration (0.4 %) of mercuric acetate are added. It is clear from this Table that the effect for the concentration of $AgNO_3$ is exceedingly slight in comparison with the variation of concentration of mercuric acetate.

Accordingly, it is evident that the concentration of silver nitrate governs the absorption rate of ethylene and the concentration of mercuric acetate controls the irreversibility of absorption of ethylene. The formation of pulverized noble metal alloy from the mixed solutions of silver nitrate and mercuric nitrate at room temperature has been reported.[8] It is assumed that silver ion may be combined with mercuric ion in this reagent but ethylene attacks silver ion and migrates into mercuric ion. The complex between ethylene and mercuric salt is known to be formed.[9]

The irreversibility of absorption of ethylene can be explained by the stability of this complex.

Summary

A mixed solution of silver nitrate and mercuric acetate absorbs ethylene most rapidly. The concentration of silver nitrate governs the rate of absorption of ethylene and the concentration of mercuric acetate controls the irreversibility of absorption of ethylene. For the determination of ethylene, an aqueous solution of 2.5 % these salts is enough satisfactory.

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