THE HYDROLYSIS OF NAPHTHOL ETHERS.

By Gopal Balkrishn Kolhatkar, Professor of Chemistry in the Ferguson College, Poona.

I. INTRODUCTION.

The alkyl ethers derived from both aliphatic and aromatic hydroxyl compounds are usually regarded as much more stable than the esters of organic acids. As a rule they cannot be prepared by a method analagous to the catalytic esterification of acids, and when formed are much more resistent to the action of hydrolysing agents.

W. A. Davis (J. C. S. 1900, 79, 33) has shown, however, that 90-95 per cent yields of methyl, ethyl and propyl ethers of beta-naphthol can be obtained by heating the naphthol, alcohol and sulphuric acid in the relative proportions by weight 2 : 2 : 0·8 during 12-20 hours at 100°.

Gattermann (Annalen, 1888, 244, 72) had recommended a similar method for the preparation of the methyl and ethyl ethers of alpha-naphthol, but Weit and Schneider (Ber., 1901, 34, 3173) state that the method is not adapted to large scale work, as the reaction is a balanced one and the yields of ethers are by no means theoritical.

No experiments appear to have been made in order to ascertain what yields of ethers are formed when the ordinary Fischer-Speier method of esterification is used. An experiment with beta-naphthol and a 5% solution of hydrogen chloride in methyl alcohol showed the formation 30-40 per cent. of methyl ether after three hours.

The action of both mineral acids and alkalis as hydrolysing agents on the ethers of alpha and betta naphthols has been examined. The ethers are very resistent to solutions of alkali hydroxides but can be hydrolysed to an appreciable extent when heated with concentrated hydrochloric acid at 100°.

It is clear that the naphthol ethers stand somewhat intermediate between the phenolic ethers and the esters of carboxylic acids as regards both their catalytic formation and their

decomposition by mineral acids. Their similarity to phenolic ethers is shown by their resistance to the hydrolysing power of alkali hydroxide solutions.

II. Experimental.

(a) *Estimation of naphthols in presence of their ethers.* The naphthol ethers used in the experiments were prepared according to Gattermann's method and then carefully purified. The methyl ether of beta-naphthol was purified by crystallisation from methyl alcohol and the ethyl ether by fractional distillation under reduced pressure. Methyl and ethyl ethers of alpha-naphthol retain tenaciously small amounts of the naphthol. (compare Witt and Schneider *loc. cit*). Traces of naphthol were therefore removed by treatment with diozobenzene-sulphonic acid in the presence of an alkali, and the ether after removal of the tetrazo-colour was purified by distillation under reduced pressure. Anisole was prepared by the action of methyl iodide on sodium phenoxide and then carefully rectified.

In the investigation, as it would be necessary to estimate small amounts of naphthol and phenol alone or in the presence of their ethers, the following different methods of estimating them were tested with a view to ascertain their delicacy.

I. Ordinary ethyl ether was carefully purified till 100c.c. distilled off from a weighed flask left a residue weighing less than a milligram.

Weighed amounts of pure sublimed naphthols were then mixed with their ethers. The naphthol ethers were eliminated by extraction with ethyl ether from an alkaline solution. The solution was acidified and the naphthols taken up with ether. The etheral solution was dried and transferred to a weighed flask. The ether was distilled off at as low a temperature as possible and the residual naphthol was dried to constant weights in a vacuum dessicator. The oxidation that the naphthols undergo in alkaline solution, their volatile character, and other causes introduced considerable error in the estimations of naphthols by this method of direct weighing, the error often amounting to as much as 5 per cent.

As no better method could be found this process was used for estimating alpha-naphthol when mixed with its ethers.

2. Estimation of naphthols by a saturated solution of picric acid (Kuster Ber., 1894, *27*, 1101). With pure sublimed naphthols

good results were obtained as shown by the following table :—

	Amount taken	Amount estimated.
alpha-naphthol	0·2038	0·206
	0·198	0·194
	0·0304	0·0312
beta-naphthol	0·220	0·2217

Naphthols mixed with ethers cannot, however, be estimated directly by this method. When freed as far as possible from ether as detailed in (1) and the etheral residue digested with a saturated solution of picric acid, a far longer time was required for the formation of the additive compound. Further in the case of alpha-naphthol a small amount of the residue did not combine with picric acid even after digestion for a long time. The method thus gave rise to errors even greater than those given by method (1).

3. Estimation of beta-naphthol by titration in a neutral, or a solution slightly acidic with acetic acid, with a diazotised solution of para-nitraniline as recommended by Schwalbe (Ber., 1905, *38*, 3072.)

The preparation of the diazo-solution will be clear from the following :—

0·239 gram of paranitraniline was carefully weighed out and dissolved in about 5 c. c. of 2 N. hydrochloric acid. The solution was then cooled in ice and added gradually to an ice cold solution of 0·125 gram of pure sodium nitrite in 10 c. c. of water. Any para-nitraniline adhering to the beaker was washed with 3·5 cc. of 2 N. hydrochloric acid and then with a little water. (The sodium nitrite solution should not be added to the p-nitraniline because the diazo solution first formed combines with the excess of p-nitraniline and gives rise to a yellow precipitate of diazo-amino-compound in varying amounts). The slight excess of nitrite is tested by starch iodide paper. The diazo-solution so prepared is poured into a 100 cc. flask, 1·75 grams of sodium acetate is added to replace the hydrochloric acid by the weak acetic acid and the whole made up to 100 c. c. The diazo solution so prepared is fairly stable and decomposes to the extent of only about 2 per cent in 24 hours.

This method when carefully carried out gives excellent results as the following table shows :—

Amount of beta-naphthol taken	Amount estimated
0·1819	0·1814
0·1565	0·1562
0·1085	0·1080
0·1164	0·1168

While estimating the naphthol by this method it was observed that the methyl and ethyl ethers do not react with the diazo solution under the given conditions. To verify this point beta-naphthol mixed with its ether was estimated by this method with the following results :—

Amount of beta-naphthol present (mixed with its ether)	Amount estimated
0·1017	0·1022

The tedious process of separating the naphthol ethers by extraction with ordinary ether and errors incidental to the process could thus be avoided. I therefore followed this method for estimating beta-naphthol in the experiments detailed below :—

4. Phenols were estimated in alkaline solution by means of iodine (Messinger and Vortmann, Ber., 1890, *23*, 2754.) Here also it was observed that anisole does not appreciably react with iodine solution under the conditions of the experiments and therefore the phenols could be estimated by this method in the presence of their ethers with tolerable accuracy as the following determination will show.

Amount of phenol present (mixed with its ether)	Amount estimated.
0·0242	0·0233

(b) *Experiments on hydrolysis.*

The methyl ether of beta-naphthol was at first heated with excess of hydrochloric acid (1 : 1) in a flask provided with a reflux condenser. Varying amounts of ether, however, sublimed into the condenser and duplicate experiments did not give concordant results.

The next series of experiments were made by heating the ether mixed with hydrochloric acid (1 : 1) in small flasks. The flasks were closed with a rubber stopper and in the stopper was inserted a small glass tube capable of being moved airtight backwards and forwards. The lower end of the tube was sealed and at a distance of about 1½ cm. above the sealed end a small hole was blown in it. At first the glass tube was so arranged that the hole connected to the inside of the flask. The flask was then evacuated and when fairly exhausted the tube was carefully drawn out (while still attached to the pump) till the sealed end was flush with the under surface of the stopper, when the connection with the pump was broken. If the stopper and the tube are well chosen the vacuum can be kept for a long time. The flasks were heated on a

boiling water bath and were occasionally shaken to prevent the ethers from subliming on the rubber stopper. Duplicate experiments yet differed considerably as will be seen from the table I :—

TABLE I.

Time in hours	Amount of ether taken in grams.	Volume of acid used. in C. C.	Amount of naphthol estimated in grams.	Percentage of ether hydrolysed.
4	0·3922	78·5	0·120	33·45
4	0·3930	78·5	0·142	39·79
2	0·4479	89·4	0·075	18·45
2	0·4380	87·6	0·079	19·52

The following experiments illustrate the effect of shaking on the rate of hydrolysis. The re-action mixtures were introduced into glass tubes which were evacuated and sealed. One of the tubes was constantly shaken in a boiling water bath while the other was shaken once every half hour.

TABLE. II.

	Time in hours.	Amount of ether taken.	Volume of acid in C. C.	Amount of naphthol estimated.	Percentage of ether hydrolysed.
Constantly shaken.	4	0·5002	9·2	0·055	12·08
Shaken occasionally.	4	0·4996	9·0	0·028	6·27

These results clearly show that shaking the reaction mixture has a marked effect on the decomposition. A suitable stirring apparatus was therefore devised in order that all tubes should be shaken at the same rate. Bulbs of about 40 c. c. capacity were blown on glass tubes, and after introducing the acid

and the ether they were drawn out, evacuated, sealed, placed in the boiling water bath and constantly stirred at the rate of one backward and forward movement once every two seconds. The accompanying table shows some of the results obtained by this method.

TABLE III.

Ether of beta-naphthol taken.	Time in hours.	Amount of ether taken	Volume of acid 5 3 N. in C. C.	Amount of naphthol estimated.	Percentage of ether hydrolysed.
Methyl ...	4	0·1400	18·4	0·0940	73·7
,, ...	4	0·1385	18·23	0·0945	74·9
,, ...	4	0·1577	18·87	0·0950	66·0
,, ...	4	0·3140	18·7	0·1010	35·3
,, ...	4	0·3140	18·8	0·1030	36·0
,, ...	2	0·1574	18·7	0·0525	36·3
,, ...	2	0·1580	18·7	0.0535	37·1
,, ...	2	0·0786	18·9	0·0534	74·6
,, ...	2	0·0784	18 9	0·0525	73·5
Ethyl ...	4	0·1914	18·9	0·0427	26·0
,, ...	4	0·1917	18·9	0·0425	26·0

The above results are fairly concordant. They also show that the amount of the ether has only a slight influence on the decomposition. The decomposition obviously depends upon the strength of the acid and its volume.

To secure comparable data the acid used in the following experiments was exactly five times normal, the volume of the acid used was exactly 20 c. c. or some multiple of this and the amount of ether taken represented roughly ·001 gram mol. or a multiple of this.

The results obtained are given in Table IV.

TABLE IV.

	Time in hours.	Amount of ether taken	Volume of acid in C. C.	Amount of naphthol estimated.	Percentage of ether hydrolysed.
Methyl ether of beta-naphthol	4	0·1610	20	0·0860	58·8
	4	0·1620	20	0·0880	59·7
	4	0·1606	10	0·0463	31·7
	4	0·1572	10	0·0469	32·8
	4	0·3151	20	0·0956	33·4
	8	0·1560	10	0·0855	60·2
Ethyl ether of beta-naphthol	4	0·1735	20	0·0355	24·4
	4	0·1715	20	0·0363	25·3
Methyl ether of alphanaphthol	4	0·1568	20	0·0200	14·0
	8	0·3263	40	0·0770	25·9
Anisole	4	0·1190	20	0·0027	2·6
	4	0·1050	20	0·00224	2·5

III. General Conclusions.

1. Ethers of beta-naphthol are much more readily hydrolysed than those of alpha-naphthol by means of hydrochloric acid. Ethers of phenol are decomposed to only a slight extent under similar conditions.

2. The methyl ether of beta-naphthol is more readily hydrolysed than the ethyl ether.

3. The reaction may be regarded as taking place between the saturated solution of the ether in the hydrochloric acid and the hydrolysing agent. With efficient shaking the consentration of the ether should remain constant so long as drops of ether remain present. Hence the amount hydrolysed should be independent of the amount of ether actually taken but should vary directly with the volume of the acid and with the time. The amount of beta-naphthol set free when 0·161 ether is taken is 0 086, by increasing the ether to 0·3151 i. e. nearly doubling the amount the weight of naphthol set free is only 0·0956 i. e. is increased by about 12 per cent.

4. The decomposition is roughly proportional to the volume of the acid used.

5. The decomposition is also approximately proportional to the time of the reaction.

6. The strength of the acid used has a very great influence on the extent of the decomposition. 5·3 N. acid produces 0·095 gram of napthol while 5 N. acid under the same conditions only liberates 0·086 gram.

CHEMICAL LABORATORY,   DEPT. OF GENL. & ORG. CHEM.
    FERGUSSON COLLEGE,   INDIAN INSTITUTE OF SCIENCE,
            POONA.   BANGALORE.