Dehydration of Alcohols with Alkali Metal Alcoholates

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THE preparation of nearly anhydrous alcohol by fractionation of mixtures of aqueous alcohol and benzene, whereby the water is removed as a ternary azeotrope with alcohol and benzene, is well known and widely used on the large scale. A variety of other methods for the dehydration of alcohol have been proposed, such as the use of anhydrous calcium chloride, the use of glycerol alone or in combination with hygroscopic salts, the use of metallic calcium, aluminum, or magnesium, etc. None of these other processes has met with the success of the distillation method in the presence of a liquid which yields an azeotropic mixture owing to the economy of operation which the latter process permits. The distillation process, however, reaches its maximum efficiency only on very large-scale operation, where continuous operation and automatic control can be applied.

DEHYDRATION OF ALCOHOL BY ALKALI SALTS OF MONO- AND POLYHYDROXY ALCOHOLS[1]

The work described here was done in an attempt to find a method more suitable for comparatively small-scale production than dehydration by means of benzene. Glycerol, potassium carbonate, triethanolamine, and ethylene glycol were all tried. Although the alcohol was increased in strength, none of these substances gave better than a 97.4 weight per cent alcohol on one treatment. A 98.6 weight per cent alcohol was obtained in two stages from 92.5 weight per cent alcohol, using glycerol and potassium carbonate.

It then occurred to the senior author to use the salts of higher alcohols or of the glycols as dehydrating agents. These salts were prepared by the usual method of mixing an excess of the alcohol with an alkali hydroxide and driving off the water (*1-3*). The aqueous ethyl alcohol was then mixed with the solutions of the anhydrous salts, and a portion was distilled off through a short column. The following salts were tried: sodium salts of glycerol, ethylene glycol, benzyl alcohol, methylcyclohexanol, *n*-amyl alcohol, xylenol, and phenol; the potassium salts of ethylene glycol and benzyl alcohol; and the calcium salts of ethylene glycol.

The reaction may be represented as follows:

$$ROX + H_2O \longrightarrow ROH + XOH$$

where R = alkyl or aralkyl radical
X = an alkali such as sodium, potassium, etc.

The amount of the salt of the alcohol or glycol taken is in excess of that necessary to react with the amount of water present in the alcohol.

COMPARATIVE DEHYDRATION EFFECT OF VARIOUS SUBSTANCES

The efficacy of the various substances tried is compared in Table I. These tests were made by mixing the indicated amount of dehydrating agent with the indicated amount of weak alcohol. The mixture was then fractionated, using a 2-foot Vigreux column, and a first fraction was collected to the amount shown in the fifth column. The alcohol content was determined from the specific gravity and is reported as weight per cent.

In addition to the above dehydrating agents, the potassium salt of ethylene glycol was prepared, but so much foaming took place while the water of reaction was being distilled that no further work was done with the potassium salt.

TABLE I. EFFICACY OF VARIOUS DEHYDRATING AGENTS

Dehydrating Agent	Amount Used	Strength of Weak Alc. Added	Strength of Alc. Added	Strong Alc. Recovered	Strength of Recovered Alc.	Remarks
		Cc.	%	*Cc.*	%	
Glycerol	100 cc. (95%)	500	92.3	400	93.6	Glycerol not dehydrated before use
Glycerol	70 cc. (95%)	350	93.6	260	94.6	Glycerol not dehydrated
Glycerol	100 cc.	500	92.3	400	94.6	Glycerol dehydrated with toluene before use
Glycerol	70 cc.	350	94.6	255	96.0	Dehydrated glycerol used
Glycerol	250 cc.	500	92.3	400	95.8	Dehydrated glycerol used
Glycerol	175 cc.	350	95.8	300	97.4	Dehydrated glycerol used
Glycerol	100 grams	500	92.5	300	94.5	Distd. through 3-ft. column
K_2CO_3	80 grams	500	92.3	400	94.2	.....
K_2CO_3	56 grams	350	94.2	348	95.3	.....
Triethanolamine	100 cc.	500	92.3	400	93.7	Triethanolamine dehydrated *in vacuo* to 130° C.
Diethylene glycol	90 grams	350 grams	92.5	200	93.8	Diethylene glycol dehydrated by boiling *in vacuo*
Ethylene glycol	200 grams	500	92.5	200	94.9	Ethylene glycol previously purified by fractionation
Glycerol + K_2CO_3	100 cc.(dry) + 100 grams (dry)	300	92.3	200 65	97.1 94.3	.....
Glycerol + K_2CO_3	100 grams (anhydrous) + 100 grams (anhydrous)	500	92.5	480	96.2	Some decomposition of glycerol during alc. distn.
Glycerol + K_2CO_3	100 grams (anhydrous) + 100 grams (1% H_2O)	500	92.5	465	97.2	Mixt. agitated during distn; distn. carried out in water bath; short fractionating column used
Glycerol + K_2CO_3	75 grams (anhydrous) + 75 grams (1% H_2O)	375	97.2	350	98.6	Same procedure as in previous expt.
Glycerol + NaOH	368 grams + 80 grams	600	92.5	500	96.5	Water removed from dehydrating mixt. by heating to 150-160° C. for 2 hours; mixt. had bad tendency to foam
Ethylene glycol + NaOH	248 grams + 165 grams (48.4% soln.)	500	92.5	400 70	97.6 94.7	Water removed from dehydrating mixture by distn. through short column until vapor temp. of 180° C. was reached; mixt. did not foam

[1] A patent application for this method is now pending.

TABLE I. EFFICACY OF VARIOUS DEHYDRATING AGENTS
(*Continued*)

DEHYDRATING AGENT	AMOUNT USED	WEAK ALC. ADDED	STRENGTH OF ALC. ADDED	STRONG ALC. RECOVERED	STRENGTH OF RECOVERED ALC.	REMARKS
		Cc.	%	*Cc.*	%	
Dry mixt. from previous expt.	260 cc.	375	97.6	300 75	99.2 94.7	Mixt. used dehydrated as above by distn. to vapor temp. of 180° C.
Benzyl alc. + Na salt of benzyl alc.	300 grams	350	92.5	300	96.0	Dehydrating mixt. prepared by mixing 4 moles benzyl alc. + 2 moles NaOH, and distg. to vapor temp. of 195° C.
Methylcyclohexanol + NaOH	295 grams 78 grams (48.4%)	238	92.5	200	95.3	Dehydrating mixt. prepared in manner similar to that used for Na salt of ethylene glycol; mixt. was dark brown after dehydration and practically insol. in alc.
n-Amyl alc. + NaOH	352 grams 160 grams (50%)	500	92.5	400	94.7	Dehydrating mixt. prepared by distng. through column and separating water from amyl alc.; mixt. distd. until vapor temperature reached 125° C.
Xylenol + NaOH	488 grams 160 grams (50% soln.)	500	92.5	400	94.9	Water removed from dehydrating mixt. by distn.; mixt. became dark on heating
Phenol + NaOH	376 grams 178 grams (50% soln.)	500	92.5	400	95.0	Water removed from mixt. by distn.
Benzyl alc. + KOH	432 grams 112 grams (dry)	500	92.5	400	95.7	Water of reaction removed from dehydrating mixt. by distn. to vapor temp. of 170° C.
Ethylene glycol + K_2CO_3	100 grams 100 grams	500	92.5	470	96.1	.....
Ethylene glycol + $Ca(OH)_2$	248 grams 55 grams	450	92.5	400	95.3	Water of reaction distd. from dehydrating mixt. before use.

DEHYDRATING ACTION OF SODIUM ETHYLENE GLYCOLOXIDE

The three best dehydrating agents tried, as can be seen from Table I, were the mixtures of glycerol and potassium carbonate, of ethylene glycol and potassium carbonate, and of ethylene glycol and its sodium salt. All three of these gave strong alcohol in two steps starting with 92.5 per cent alcohol, but because there was decomposition of glycerol, the glycerol–potassium carbonate mixture was not tried out further. The mixture of ethylene glycol and its sodium salt showed promise of being a good dehydrating agent.

In order to determine whether the mixture of ethylene glycol and its sodium salt could be used repeatedly for alcoholic dehydration without any deterioration, a series of runs was made with the same batch of dehydrating agent. Two-hundred and forty-eight grams of ethylene glycol and 160 grams of 50 per cent sodium hydroxide were charged to a glass flask equipped with a Vigreux column, the water was removed by distilling to a vapor temperature of 180° C., and the cycle was repeated. The proportions of alcohol used contained water equivalent to 80 per cent of that which theory requires to react with the glycoloxide; previous experimentation had shown that this was the best proportion. The ethylene glycol which distilled with the water during the dehydrations was recovered by fractionation and charged back to the dehydrating mixture. The results on the series of ten batches run are given in Table II.

TABLE II. RESULTS OF REPEATEDLY DEHYDRATING ALCOHOL WITH MIXTURE OF ETHYLENE GLYCOL AND ITS SODIUM SALT

BATCH	DEHYDRATING MATERIAL	92.5% (WEIGHT) ALCOHOL CHARGED	STRONG ALCOHOL RECOVERED	COMPOSITION BY WEIGHT	WATER FRACTION
	Grams	*Cc.*	*Cc.*	%	*Cc.*
1	257	500	473	97.3	35
2	257	500	470	97.0	40
3	270	500	470	96.8	23
4	260	500	470	96.8	42
5	265	500	470	96.9	43
6	262	500	470	96.9	44
7	260	500	470	96.5	49
8	263	500	470	96.6	40
9	253	500	470	96.8	31
10	250	500	470	96.8	..

Before taking the water fraction from batch 1, there were added 20 cc. of glycol, which had been recovered by fractionation from the water removed from the initial preparation of sodium glycoloxide. Before taking the water fraction from batch 4, there were added 12 cc. of glycol, recovered from the water fractions of batches 1, 2, and 3. The same procedure was followed on batch 7, 14 cc. of glycol recovered from the water fractions of batches 4, 5, and 6 being added. Before starting batch 10, there were added 11 cc. of glycol recovered from the water fraction of batches 7, 8, and 9.

EFFECT OF METAL EQUIPMENT

In order to determine the effect of metal equipment on sodium ethylene glycoloxide, a series of runs similar to that described above was made in iron and in copper. In iron, the decomposition of the glycoloxide was quite rapid, and practically all of the glycol was decomposed after four successive batches. In the case of copper, the decomposition was less marked, but became apparent after about seven successive batches.

It was thought that this decomposition was accelerated by the high temperature which was required to dehydrate the glycoloxide. In order to obviate the use of a high temperature, a series of runs was made in copper similar to that described above, with the difference that the residue remaining after the strong alcohol had been distilled off was dehydrated under a vacuum in such a way that the temperature did not go over 150–155° C. A series of twenty-five batches was made in this way, with the following results:

Material charged	496 grams glycol 333 grams 48.1% NaOH 19775 grams 92.0% (by weight) alcohol
Material obtained	541 grams sodium ethylene glycoloxide residue 1591 grams water fraction 849 grams middle alcohol fraction (92.0% by weight) 17494 grams strong alcohol fraction (97.0% by weight)
Loss in 25 runs	129 grams

The glycol was recovered from the water fractions by fractionation, and from the glycoloxide residue by acidification and distillation. The total recovery was 416 out of 496 grams charged, or 84 per cent of the original charge. This apparent difference includes the unavoidable mechanical losses incurred in handling the recovered glycol over the whole

series of experiments. It is believed that consumption of glycol can be materially decreased in larger-scale operation.

Adaptation to Continuous Process

The dehydrations described previously were all made as separate batch experiments. Laboratory experiments were then made in order to determine whether this method of dehydration could be adapted to continuous operation. For this purpose it was necessary to add an excess of glycol to the glycoloxide in order to bring the crystallizing point of the glycol-glycoloxide mixture down below the boiling point of alcohol. A mixture of 5 moles of ethylene glycol to 2 moles of sodium hydroxide when dehydrated, crystallized at about 95° C.; a mixture of 6 moles of glycol to 2 moles of sodium hydroxide crystallized at about 60° C.; and a mixture of 7 moles of glycol to 2 moles of sodium hydroxide was still fluid at 40° C. The last named mixture was used in the continuous experiment.

Alcohol (92.5 per cent by weight) was boiled in a glass still, and the vapors were passed up a packed column 4 feet long. The dehydrating mixture was added to the column at a point about 1 foot from the top, at the rate of 150 grams for every 100 cc. of alcohol distillate collected. After a little time had been allowed for the system to reach equilibrium, two successive 100-cc. portions of the distillate were collected separately and analyzed. One of these was 99.5 per cent (by weight) alcohol, and the other was 99.2 per cent.

This experiment serves to show that 99 per cent alcohol can be obtained by a continuous process with sodium ethylene glycoloxide. In large-scale operation, of course, the aqueous alcohol would be fed to the column at a point near the bottom while a reboiler at the bottom of the column would supply the necessary heat. The dehydrating mixture would be continuously drawn off and dehydrated under vacuum in a separate system.

Application to Dehydration of Other Alcohols

The principle of dehydration with sodium ethylene glycoloxide was applied to *tert*-butyl alcohol and to isopropyl alcohol. In the former case, starting with commercial *tert*-butyl alcohol which had a specific gravity of 0.80560 at 25°/25° C., and which would not crystallize at 0° C., it was possible to obtain alcohol of crystallizing point 18° C. and specific gravity of 0.78254. Starting with isopropyl alcohol of specific gravity 0.80884 at 25° C., it was possible to obtain a dehydrated product with specific gravity 0.78714 at 25° C.

Summary and Conclusion

The alkali salts of high-boiling alcohols, glycols, and glycerol can be used for the dehydration of the lower-boiling alcohols which are difficult to dehydrate by ordinary means.

Sodium ethylene glycoloxide is an efficient dehydrating agent for aqueous alcohols, and has the merit that it can be readily regenerated for repeated use. The only feature which would apparently militate against its use on the large scale is the gradual decomposition which takes place in presence of some metals, resulting in ultimate loss of the glycol. This decomposition can be minimized by the avoidance of high temperatures in the dehydration, by the use of partial vacuum, or by operation in containers which do not have a catalytic effect on the decomposition of the alcoholate.

It is anticipated that the selection of the proper material for the construction of a plant employing this method will minimize the decomposition to a point where it would no longer be a serious cost factor.

Literature Cited

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Corrosion of Bronzes by Vinegar

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A NUMBER of bronzes are used in the vinegar industry, but there has been little published to show the degree of corrosion of various bronzes by this medium under various conditions. According to St. John (*5*), a considerable amount of work has been done with wrought brasses, but information dealing with foundry brasses and bronzes is incomplete and unsatisfactory. Seiler (*6*) found that a phosphor-bronze, containing 90 to 91 per cent copper, 8 to 9 per cent tin, and about 0.25 per cent phosphorus, was resistant to corrosion by tan liquors provided the metal was free from iron, lead, and zinc. Philip (*3*) attributed the corrosion of common brass to local zinc-copper couples on the surface of the metal. Benik (*1*) stated that the corrosion product of an acid-resisting bronze was proportional to the time of immersion. Mrak and Cruess (*2*) found that a tin-copper bronze corroded faster in citric acid than in tartaric acid, and that corrosion in pure acids was faster than in tomato, lemon, or grape juices.

In order to determine the corrosion resistance of several bronzes that have been used or been recommended for use in the vinegar industry, eight bronzes and their chief components (copper, tin, and lead) were exposed under three sets of experimental conditions—namely, in still, aërated, and sprayed vinegar. These three test conditions were used, since Rawdon and Groesbeck (*4*) have shown that metals corrode differently when exposed to different corroding conditions.

Method and Apparatus

The metals used were cut into strips 5.5 × 2.5 × 44.7 mm. The copper, tin, and lead strips were but 0.6 mm. in thickness. The metals were cleaned by burnishing with a cloth burnisher and then washing in ether and alcohol, after which they were dried in a desiccator over $CaCl_2$ and then weighed just before using in the corrosion tests. The composition of the bronzes used is given in Table I.

Table I. Composition of Bronzes

Bronze	Metal								
	Cu	Sn	Pb	Zn	P	Fe	Al	Mn	C
	%	%	%	%	%	%	%	%	
1	80.00	20.00	...	..	..	..	..	..	..
49	80.00	10.00	10.00	..	..	..	..	..	..
47	75.00	10.00	15.00	..	..	..	..	..	..
44	70.00	5.00	25.00	..	..	..	..	..	..
12	85.00	5.00	5.00	5.00	..	..	..	..	..
22	85.90	8.00	6.00	..	0.10	..	..	..	..
66	86.00	10.00	...	..	..	4.00	..	..	+
69	88.98	...	...	..	0.02	2.50	4.50	4.00	..

Cider vinegar, standardized to 4.27 per cent acid as acetic by the addition of distilled water or glacial acetic acid, was used in these tests.