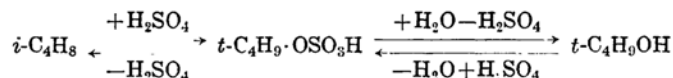


Synthesis of Tertiary Butyl Alcohol by the Hydration of Isobutylene. II. Separation of Tertiary Butyl Alcohol by the Distillation of Diluted Sulphuric Acid Solution, and on the "Porous Substance Effect", "Stirring Effect" and "Agitation Effect".⁽¹⁾

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The product of the absorption of isobutylene by sulphuric acid without polymerisation has been considered to be composed of the following equilibrium mixture.⁽³⁾



For the separation of tert-butanol from the mixture, it is in general neutralised with alkali before distillation, in order to avoid the regeneration and the polymerisation of isobutylene.⁽²⁾ tert-Butanol can be separated almost quantitatively by this method, the yield amounting to about 95% of the theoretical.⁽³⁾

In the present investigation, separation of tert-butanol from the absorption product of isobutylene without neutralising sulphuric acid with alkali has been attempted. It is described in a patent⁽⁴⁾ that about 80% of tert-butanol can be separated by the rapid steam distillation of tert-butanol from 35–40% aqueous sulphuric acid solution. In the present investigation, tert-butanol has been distilled from the absorption product of isobutylene with sulphuric acid after dilution with water to varying concentrations, and it has been observed that under optimum conditions, tert-butanol can be separated in about 60–80% theoretical yields with small regeneration of isobutylene. It has been observed that the regeneration of isobutylene increases markedly by the addition of the powder of porous substances such as pumice powder. Its mechanism has been discussed, and the analogous phenomena, observed in the other cases, have been summarised by the term "agitation effect."

Experimental Apparatus and Procedure. 1. *Absorption of Isobutylene:* The apparatus used was the same as that used in the polymerisation of isobutylene⁽³⁾, which is simpler than that used in the 1st

(1) This paper is the 7th report on the hydration of olefins to alcohol. M. Katuno, *J. Soc. Chem. Ind. Japan*, **43**(1940), 5B, 8B, 11B; **44**, 275B, 279B, 392B.

(2) Butlerow, *Ann.*, 1876, **180**, 246; 1877, **189**, 48; Read and Priestley, *J. Am. Chem. Soc.*, 1924, **46**, 1512; L. Vanino, *Präparative Chem.*, 1923, Bd. 2, S. 36, etc.

(3) M. Katuno, *J. Soc. Chem. Ind. Japan*, 1941, **44**, 102B.

(4) B. T. Brooks, U.S.P. 1,904,200 (1933); *Ind. Eng. Chem.*, 1935, **27**, 286.

report⁽⁵⁾ on the hydration of isobutylene. Isobutylene was absorbed by 67% aqueous sulphuric acid solution (143 g.) below 20°C. with vigorous stirring, accompanied by a little polymerisation, in a three necked flask. In most cases, about 50–65 g. of isobutylene was absorbed, and the amount was known from the increased weight of the flask.

2. *Dilution with Water*: The absorption product was then diluted with varied amount of water with vigorous stirring below 20°C. The amount of water which was to combine with isobutylene into tert-butanol, and to be distilled with it forming azeotropic mixture (b.p. 79.9°C.; H₂O:11.76%) was added in excess, and the amount of water to be added to the absorption product of isobutylene, using 143 g. of 67% acid, was calculated by the following formula:

$$\begin{aligned} \text{Amount of water to be added (c.c.)} &= (100 \times \frac{R_{H_2O}}{R_{H_2SO_4}} - 43) \\ &+ (\text{amount of absn. of } i\text{-C}_4\text{H}_8) \times \left(\frac{18}{56} + \frac{74}{56} \times \frac{11.8}{88.2} \right) \\ &= (100 \times \frac{R_{H_2O}}{R_{H_2SO_4}} - 43) + 0.498 \times (\text{Amt. of absn. of } i\text{-C}_4\text{H}_8). \end{aligned}$$

The ratio R_{H₂SO₄}:R_{H₂O} (by wt.), or the dilution concentration of acid, represents the ratio of H₂SO₄ and H₂O by weight, which is to be realised when tert-butanol has been completely distilled off from the mixture as ideal azeotropic mixture (H₂O:11.76%).

3. *Separation of tert-Butanol by Distillation*: The diluted product was distilled in most cases using an ordinary branched flask, without using fractionating column, in the presence of a piece of unglazed porcelain to avoid bumping. The distillate was collected in a conical flask, which was attached tightly to the adapter, which has a branch tube. The branch tube of the adapter was connected to the gas holders of Mariotte bottle type,⁽⁶⁾ of about 10 l. content, to collect gas by substituting saturated solution of sodium chloride. The outlet of the gas in the Mariotte bottle was kept under slightly lower pressure than atmospheric, by about 1–2 cm. height of saturated NaCl solution.

The distillation was carried out collecting the gas formed, and was continued for some time after having almost distilled tert.-butanol to complete its distillation. The volume and pressure of the gas collected was measured, and was analysed for isobutylene by absorbing with 87% sulphuric acid. The amount of isobutylene collected was, however, not the total amount of isobutylene formed, a considerable amount remaining in the space of the distillation apparatus.

The distillate, composed of dilute aqueous solution of tert.-butanol and polymerised oil, was then separated from polymerised oil by the same treatment as described in the previous paper.⁽⁵⁾ The aqueous solution of tert.-butanol was then distilled through 30 cm. Widmer column, till

(5) M. Katuno, *J. Soc. Chem. Ind. Japan*, **44**(1941), 392B.

(6) Cf. M. Katuno, *J. Soc. Chem. Ind. Japan*, **41**(1938), 75B.

water distils at its boiling point after complete distillation of aqueous azeotropic mixture of tert.-butanol. The yield and density (d_4^{20}) of the distillate was measured, and the yield of tert.-butanol was calculated comparing with the density of tert.-butanol-water system.⁽⁷⁾

4. *Materials:* Isobutylene: Commercial extra pure isobutanol was dehydrated with activated alumina below 400°C., generally at about 370–380°C., and the isobutylene formed was stored in a gas holder of about 1 m³ content.

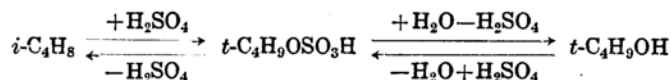
Experimental Results. The results are summarised in Table 1. When the absorption product of isobutylene was diluted to the dilution concentration of less than 30% ($\text{RH}_2\text{SO}_4:\text{RH}_2\text{O} < 30:70$ by weight; see experimental part), tert.-butanol is distilled in the theoretical yield of about 68–80% with slight regeneration and polymerisation of isobutylene (Expt. DB318, DB347 and DB 37). However, by the dilution of the acid to $\text{RH}_2\text{SO}_4:\text{RH}_2\text{O} = 40:60$ (DB 312) or 50:50 (DB 314), the regeneration of isobutylene increases markedly, and the polymerisation of isobutylene also increases in the latter case with decreasing yield of tert.-butanol (59% and 42%, respectively).

The increase in the amount of isobutylene absorbed by a definite amount of 67% sulphuric acid (143 g.), from 58 g. (DB318) to 96 g. (DB315), increases the regeneration of isobutylene, from 9.6% to 15.8%, with decrease in the theoretical yield of tert.-butanol, from 74% to 68%.

The use of fractionating column in the distillation also increases the regeneration of isobutylene (DB 310), probably due to the partial return of vaporised tert.-butanol into the acid phase to increase the chance of the dehydration into isobutylene.

All other distillations described before were carried out in the presence of a piece of unglazed porcelain, in order to avoid the bumping. The addition of 5 g. of pumice powder in the acid phase in the distillation causes a marked increase in the regeneration of isobutylene, to about 44–45% (DB 313, DB 350), with the decrease in the yield of tert.-butanol to about 43–46% of theoretical. This fact shows that the existence of a large amount of the sources of foams in the liquid phase is unfavourable for the distillation of tert.-butanol, as discussed later.

Discussions of the Results. 1. *Comparison with the "Indirect Polymerisation"*⁽⁸⁾ of isobutylene: The absorption product of isobutylene with 67% sulphuric acid or its diluted product with water may be considered to be composed of the following equilibrium mixture:



The same equilibrium mixture is also obtained by mixing tert.-butanol,

(7) Landolt Tab., 5te Aufl. Bd. I, 454, (1923) Doroshewsky, *J. Russ. Phys. Chem. Ges.*, **43**(1911), 66; Young and Fortey, *J. Chem. Soc.*, **81**(1902), 716, 735; Perno and Mieli, *Gazz.*, **37**, 11 (1907), 335.

(8) M. Katuno, *J. Soc. Chem. Ind. Japan*, **45**(1942), 181B.

Table 2.1. Separation of *tert*-Butanol by the Distillation of diluted aqueous acidic Solution.

Exptl. no.	Absorption of Isobutylene (143 μ of 67% sulphuric acid)		Dilution of the Absorption Prod.		Regenerated <i>i</i> -C ₄ H ₈ collected		Polymer ⁽¹⁾		<i>tert</i> -Butanol			Sum of the theor. yield (%)						
	Temp. (°C)	Time (hrs)	Amount absorbed (g.)	(mol.)	Water added (c.c.)	Concn. of acid after distillation of <i>i</i> -C ₄ H ₉ OH-H ₂ O (azeotr. mixt., etc. (by wt.))	Vol. of <i>i</i> -C ₄ H ₈ (0°C (1 atm.))	Content of <i>i</i> -C ₄ H ₈ (vol. %)	Yield (g.)	Theor. yield (%)	Aqueous Solution		Yield of <i>t</i> -C ₄ H ₉ OH (g.)	Theor. yield (%)				
											Yield (g.)				Yield (%)	Content of <i>t</i> -C ₄ H ₉ OH (%)		
DB37	14-18	4 ⁵⁵ / ₆₀	62.5	1.11	390	H ₂ SO ₄ :H ₂ O=20:80 (by wt.)	3.1 ₂	50	3.6 ₅	5.8	2.1	4.0	100.5	0.8663	65.5	65.8	79.0	83.4
DB347	14-17	4 ⁵⁵ / ₆₀	57.3	1.02	386	H ₂ SO ₄ :H ₂ O=20:80	2.4 ₈	48.3	2.9 ₉	5.2	3.8	6.6	129.8	0.9124	45.8	59.4	78.5	90.3
DB318	15-18	3 ⁵⁵ / ₆₀	57.5	1.02 ₅	219	H ₂ SO ₄ :H ₂ O=30:70	3.3 ₃	65.8	5.5 ₃	9.6	1.7	3.0	109.4	0.8990	51.6	56.5	74.1	87.1
DB312	14-18	5 ⁵ / ₆₀	73.5	1.31	144	H ₂ SO ₄ :H ₂ O=40:60	7.1 ₅	81.9	14.5 ₃	19.8	3.9	5.3	175.9	0.9437	32.3	56.8	53.5	83.6
DB314	16-17	4 ⁵⁵ / ₆₀	60.5	1.08	87	H ₂ SO ₄ :H ₂ O=50:50	7.3 ₃	86.7	15.8 ₁	26.2	9.9	16.3	119.9	0.9537	27.8	33.3	41.7	84.2
DB315	14-19	7 ¹⁰ / ₆₀	96	1.71	238	H ₂ SO ₄ :H ₂ O=30:70	7.0 ₂	86.6	15.2 ₀	15.8	3.1	3.2	141.8	0.8781	61.5	85.8	67.6	86.6
DB310*	14-19	5 ⁵ / ₆₀	63	1.12	221	H ₂ SO ₄ :H ₂ O=30:70	5.6 ₈	76.7	10.9 ₀	17.3	1.1	1.7	142.2	0.9277	39.2	55.8	62.1	81.1
DB313**	14-18	4 ⁵⁵ / ₆₀	51	0.91	216	H ₂ SO ₄ :H ₂ O=30:70	$\left\{ \begin{array}{l} 9.3_9 \\ 0.9_2 \end{array} \right.$	$\left\{ \begin{array}{l} 87 \\ 83 \end{array} \right.$	22.4 ₆	44.1	1.1	2.8	168.5	0.9732	18.2	30.7	45.5	92.4
DB350***	14-18	4 ⁵⁵ / ₆₀	58.0	1.03	219	H ₂ SO ₄ :H ₂ O=30:70	$\left\{ \begin{array}{l} 9.6_3 \\ 1.5_5 \end{array} \right.$	$\left\{ \begin{array}{l} 93.1 \\ 93.2 \end{array} \right.$	26.0	44.8	1.8	3.1	98.4	0.9406	33.7	33.2	43.3	91.2

(1) The polymer had a camphor-like odor in the most cases.

(2) The dilution concentration.

* Distilled with 30 cm. Widmer column.

** Distilled with 5 g. of pumice powder.

*** Distilled with 5 g. of pumice powder.

water and sulphuric acid. On heating the mixture, the equilibrium shifts to the side of dehydration to generate isobutylene, and the polymerisation or the "indirect polymerisation" takes place in the case of higher concentration of acid, as described in the previous papers⁽⁵⁾. The polymerisation becomes slow by the decrease of the concentration of acid, and only a small amount of polymer was formed with the lower concentration of acid lower than $\text{RH}_2\text{SO}_4:\text{RH}_2\text{O} \approx 40:60$. There is also the possibility that the small amount of polymer obtained was not formed in the course of distillation, but slightly in the course of the absorption of isobutylene with sulphuric acid. The regeneration of isobutylene takes place even with diluted acid, however, it decreases with the decreasing concentration of acid.

2. *The "Agitation Effect"*: It has been observed by the author in some cases⁽⁹⁾ that the side reaction of generating gas from liquid reaction mixture, where a main reaction is taking place, is promoted by the vigorous mechanical stirring or by the addition of the powder of porous substances, such as pumice⁽⁹⁾. However, the increase in the generation of isobutylene with pumice powder in the present investigation is somewhat different from the above cases in the fact that the gas or isobutylene is formed in the mere distillation of acidic tert.-butanol solution, and not as the side reaction of other main chemical reaction. It may be explained as follows. Namely, the regeneration of isobutylene takes place by the shift of the equilibrium to the side of dehydration due to the rise of temperature. When the distillation is carried out without or with only a piece of unglazed porcelain, isobutylene formed saturates and then supersaturates in the liquid phase, with only small generation of gas. The increase in the concentration of isobutylene in the liquid phase suppresses the proceeding of the reversible reaction to form isobutylene in the liquid phase. The temperature rises till the distillation takes place, increasing the vapor pressure of tert.-butanol, water etc., and tert.-butanol and water distils with relatively small formation of isobutylene.

When pumice powder is added in the liquid phase, isobutylene formed cannot supersaturate in the liquid phase, generating in innumerable foams into the gas phase, after saturation in the liquid phase. The lower concentration of isobutylene in the liquid phase promotes the rapid proceeding of the reversible reaction to form isobutylene, which successively generates into the gas phase. The distillation takes place at relatively low temperature due to the marked generation of isobutylene, which causes the distillation of tert.-butanol and water relatively small against isobutylene, due to their lower vapor pressures at the lower distillation temperature. Thus the generation of isobutylene increases with the decreasing yield of tert.-butanol by the addition of pumice powder.

The phenomenon of the increase in the formation of gaseous products from liquid reaction mixture by the addition of powder of porous substances is named now "the porous substance effect", and that by the mechanical stirring "the stirring effect", both effects being named

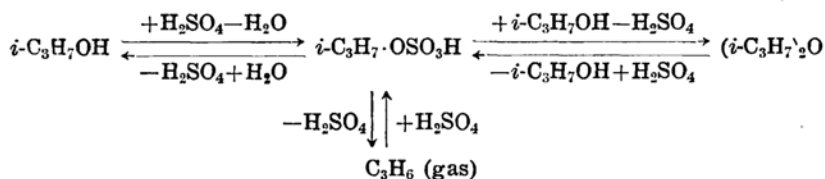
(9) M. Katuno, *J. Soc. Chem. Ind. Japan*, **41**(1938), 79B, **43**(1940), 8B, **45**(1942), 181B.

generically "the agitation effect". Some "agitation effects" hitherto observed by the author have been summarized in the following.

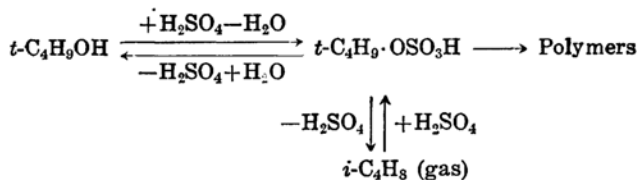
The "agitation effect" is observed when the reversible reaction B to form gaseous reaction product from liquid phase takes place parallel with the main reaction A in the liquid phase. When the reaction is carried out without stirring or addition of powder of porous substances, the gaseous reaction product of the reversible reaction B saturates and then supersaturates in the liquid phase to increase its concentration, which suppresses the proceeding of the reversible reaction B, with relatively small yield of gaseous products. The main reaction A proceeds with good yield of the product. However, when the reaction mixture is stirred vigorously or mixed with pumice powder, the gaseous reaction product cannot supersaturate in the liquid phase, due to the rapid generation into gas phase after saturation. The reversible reaction B proceeds rapidly to form gaseous product successively due to the decrease in its concentration in the liquid phase. The reaction B is promoted thus by the mechanical stirring or by the addition of powder of porous substances, with the decrease in the yield of the reaction product of A.

The examples of the "agitation effect" observed hitherto are as follows.

(1) The formation of propylene in the etherification of isopropyl alcohol with sulphuric acid ("porous substance effect" and "stirring effect")⁽¹⁰⁾. (2) The regeneration of propylene in the hydrolytic distillation of the absorption product of propylene with sulphuric acid followed by dilution with relatively small amount of water ("porous substance effect")⁽¹¹⁾. These two cases are based on the following reactions.



(3) The regeneration of isobutylene in the "indirect polymerisation"⁽¹¹⁾ of isobutylene or in the polymerisation of the mixture of tert-butanol, water and sulphuric acid. ("porous substance effect" and "stirring effect")

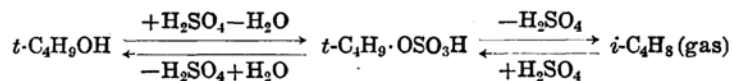


(4) The regeneration of isobutylene in the distillation of the dilute aqueous sulphuric acid solution of tert.-butanol. ("porous substance

(10) M. Katuno, *J. Soc. Chem. Ind. Japan*, **41** (1938), 77B, 79B.

(11) M. Katuno, *ibid.*, **43** (1940), 8B.

effect"). This case is somewhat different from the above three cases in the fact that isobutylene gas is formed in the mere distillation of acidic solution of tert-butanol, not accompanied with the main reaction in the liquid phase, and is based on the following reaction.



Although "stirring effect" was not tested in a few cases, mentioned above, it may be also observed accompanied with the "porous substance effect".

Summary.

1. The separation of tert-butanol by the distillation from diluted aqueous sulphuric acid solution has been studied as the method of separation of tert-butanol from the absorption product of isobutylene with sulphuric acid without neutralising acid with alkali. By the suitable dilution of the absorption product, tert-butanol can be separated in the theoretical yield of about 68–80%, with small regeneration and polymerisation of isobutylene. The regeneration of isobutylene increases and the polymerisation takes place in a considerable extent with increasing concentration of acid. The increase in the absorption of isobutylene with a definite amount of acid, or the use of fractionating column in the distillation increase the regeneration of isobutylene.

2. The distillation in the presence of pumice powder increases markedly the formation of isobutylene with the decrease in the yield of tert-butanol. An explanation has been given.

3. The marked increases in the formation of gaseous product from liquid reaction mixture by the addition of powder of porous substances, such as pumice powder, and by the vigorous mechanical stirring have been named as "the porous substance effect" and "the stirring effect" respectively, both being named generically as "the agitation effect". Some examples of the "agitation effect" observed hitherto have been summarized.

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