# Synthesis of Tertiary Butyl Alcohol by the Hydration of Isobutylene. III. Separation of Tertiary Butyl Alcohol by the Extraction with Solvents.[1]

By Masaharu KATUNO.

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As another method of separation of *tert*-butanol from the absorption product of isobutylene with aqueous solution of sulphuric acid, without neutralising acid with alkali, the extraction with solvents has been investigated. There is already a patent on such a process[2].

According to the results of the present investigation, ethyl ether is the most suitable solvent, and it is necessary to dilute the absorption product of isobutylene with 67% sulphuric acid with water before extraction in order to make *tert*-butanol readily extractable. It is remarkable that all isobutylene absorbed can be extracted as *tert*-butanol from the acidic solution, which probably suggests that the hydrolysis of *tert*-$C_4H_9OSO_3H$ is rapid and reversible, and is establishing an equilibrium state.[4] This fact is different from the case of secondary olefines, such as normal butylenes, where the secondary alcohols formed remain unextracted as stable ester, *sec*-$C_4H_9OSO_3H$, in a considerable amount[3].

**3·1. Experimental Apparatus and Procedure.** I. *Absorption of Isobutylene with Sulphuric Acid.* The procedure is almost the same as that of the previous report, except that in most cases about 100–110 g. of

(1) This paper is the 8th report on the hydration of olefine into alcohols. Previous Paper: this Bulletin, **18**(1943), 211.

(2) H. A. Guinot, *U.S.P.*, 2, 139, 953; *Chem. Abst.*, **33**(1939), 2146; Japanese patent, 140, 718 (1941).

(3) B. T. Brooks, *Ind. Eng. Chem.*, **27**(1935), 286.

(4) The previous and the next report.

Table 3·1. The Extraction of *tert*-Butanol with Solvents.

| Exptl. No. | Absorption of Isobutylene (143 g. of 67% sulphuric acid) | | | | Dilution of the Absorption Product | | Extraction | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Temp. (°C.) | Time (hrs.) | Amount absorbed (g.) | Amount absorbed (mol.) | Vol. of water added (c.c.) | $R_{H_2SO_4}$ : $R_{H_2O}$ (Weight ratio) | Conditions | $t$-$C_4H_9OH$ remained unextracted (g.) | Theor. yield of $t$-$C_4H_9OH$ calcd. (g.) | %age of extraction (%) | References |
| DB 304 | 14~19 | $4^{45}/_{60}+2^{50}/_{60}$ | 101.5 | (1.81) | 32.5 (1.8 mol.) | $H_2SO_4:H_2O = 33:67$ | 5 times with 100 c.c. $C_6H_6$ | (104~118) | 134 | (16~30) | Initial 26g. distilled at lower temp. containing $C_6H_6$ |
| DB 305 | 14~19 | $7.0+2^{45}/_{60}$ | 103.0 | (1.84) | 223 | $H_2SO_4:H_2O = 29:71$ | ,, | 35.3 | 136 | 74.0 | |
| DB 306 | 14~19 | $5^{30}/_{60}+6^{55}/_{60}$ | 102.0 | (1.82) | 223 | $H_2SO_4:H_2O = 29:71$ | 5 times with 100 c.c. $o$-$C_6H_4Cl_2$ | 73.2 | 135 | 45.8 | |
| DB 317 | 16~18 | $4^{45}/_{60}+2^{5}/_{60}$ | 102.0 | (1.82) | 223 | $H_2SO_4:H_2O = 29:71$ | 5 times with 100 c.c. $(C_2H_5)_2O$ | 12.4 | 135 | 90.8 | The initial 200 c.c. solvent mixed hemogenously with acid layer in winter |
| DB 307 | 14~18 | $6^{5}/_{60}+2^{40}/_{60}$ | 102.5 | (1.83) | 223 | $H_2SO_4:H_2O = 29:71$ | 10 times with 100 c.c. $(C_2H_5)_2O$ | ≒0 | 135.5 | ≒100 | ,, ,, ,, |
| DB 343 | 14~17 | $7^{20}/_{60}+{}^{30}/_{60}$ | 101.5 | (1.81) | 190 | $H_2SO_4:H_2O = 32:68$ | 5 times with 100 c.c. $(C_2H_5)_2O$ | 22.9 | 134 | 82.9 | ,, ,, ,, |
| DB 359 | 20~21 | $2^{45}/_{60}$ | 6.5 | (0.12) | Absorbed with 167 g. (0.5 mol. $H_2SO_4$) of 29% sulphuric acid + 3.0 g. $Ag_2SO_4$ | | | | | | |
| DB 360 | 21~22 | $7^{5}/_{60}$ | 24.8 | (0.44) | Absorbed with 125 g. (0.5 mol. $H_2SO_4$) of 38% sulphuric acid + 3.0 g. $Ag_2SO_4$ | | | | | | |
| DB 371 | 17~24 | $5^{40}/_{60}$ | 22.0 | (0.39) | Absorbed with 125 g. (0.5 mol. $H_2SO_4$) of 38% sulphuric acid + 3.0 g. $Ag_2SO_4$ | | | | | | |
| | | $8^{10}/_{60}$ | 44.3 | (0.79) | | | | | | | |
| | | $7^{10}/_{60}$ | 60.3 | (1.08) | | | | | | | |
| | | $7^{5}/_{60}$ | 71.8 | (1.28) | | | | | | | |
| | | $7^{5}/_{60}$ | 80.8 | (1.44) | | | | | | | |
| | | $7^{35}/_{60}$ | 81.1 | (1.45) | | | | | | | |

isobutylene was absorbed with 143 g. of 67% sulphuric acid (about 1 mol. of $H_2SO_4$), below 20°C. with little polymerisation[5].

2. *Extraction with Solvents.* The extraction of the absorption product with 67% acid with solvents, such as benzene, is not effective, and ethyl ether mixes homogenously with the acid layer. By the dilution of the acid to the dilution concentration of $H_2SO_4:H_2O \fallingdotseq 30:70$ (by wt.) (= 29:70 (by wt.) in detail), *tert*-butanol becomes readily extractable in most cases. Since 1 mol water combines with 1 mol isobutylene, the corresponding amount of water should be added in excess on dilution. The amount of water to be added for the dilution of the absorption product with 143 g. of 67% sulphuric acid to the dilution concentration $H_2SO_4:H_2O \fallingdotseq 30:70$ (by wt.), was calculated by the following formula:

Amount of water (c.c.) $= (100 \times \frac{70}{30} - 43) + (\text{Absorbed amount of isobutylene}) \times \frac{18}{56} = 190 + (\text{Absorbed amount of isobutylene}) \times 0.321$. The dilution was carried out with vigorous stirring below 20°C. The product was then extracted with solvents using a separatory funnel 5 times, in most cases, with each 100 c.c. solvent. In case of ethyl ether, the first one portion of 100 c.c. (in summer) or the first two portions (in winter) of ether mix with the acid layer. However, it separates into two layers by the addition of the next portion of solvent. The extracts were stored after neutralisation of the acid with excess alkali.

3. *The Separation of* tert-*Butanol remaining unextracted.* In order to know the amount of *tert*-butanol extracted, the amount of *tert*-butanol remaining unextracted in the acid phase was determined. Since it has been observed that the isobutylene absorbed can be recovered almost completely as *tert*-butanol by making the solution strongly alkaline and by distillation[6], the amount of *tert*-butanol extracted can be known readily from the difference between *tert*-butanol remaining and the theoretical amount corresponding to isobutylene absorbed.

The acid layer after extraction was diluted with water, if necessary, (DB 304), to $H_2SO_4: H_2O \fallingdotseq 30:70$ (by wt.) with stirring below 20°C. It was then treated with concentrated sodium hydroxide solution with vigorous stirring till it showed strongly alkaline, using phenolphthalein as indicator. The product was then distilled with 30 cm. Widmer column to obtain a distillation curve against the weight of distillate, collecting the distillate in a vessel placed on a rough balance[7]. *tert*-Butanol was distilled as the aqueous azeotropic mixture (b.p.=79.9°C; $H_2O$:11.76%)[8], and then the boiling point rapidly rose to that of water. In case of ether extraction a small amount of ether was distilled before *tert*-butanol-water azeotropic mixture. The boundary of two fractions in the distillation curve was defined at the point where the curve cuts the middle tempera-

(5) cf. M. Katuno, *J. Soc. Chem. Ind. Japan*, **44**(1941), 392B; **45**(1942), 102B, 181B.

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

(7) cf. M. Katuno, *J. Soc. Chem. Ind., Japan*, **45**(1942), 102B; **41**(1938), 75B.

(8) H. S. Davis and W. J. Murray, *Ind. Eng. Chem.*, **18**(1926), 844.

ture of two fractions[9]. From the amount of *tert*-butanol-water azeotropic mixture the amount of *tert*-butanol was calculated, assuming that 88.24% of *tert*-butanol was contained[8].

The difference from theoretical amount of *tert*-butanol corresponding to isobutylene absorbed was regarded as the amount of *tert*-butanol extracted, and the percentage of extraction against the theoretical amount of *tert*-butanol was calculated.

4. *Preliminary Experiments on the Extraction with various Solvents.* Since it is very troublesome to test various solvents by the absorption of isobutylene with sulphuric acid with subsequent dilution and extraction, preliminary experiments were made to know roughly the ability of various solvents for the extraction of *tert*-butanol. In the present preliminary investigation, isopropyl alcohol, which is known to have physical properties resembling those of *tert*-butanol[10], was extracted from aqueous solution, as the model experiment for the extraction of *tert*-butanol from aqueous sulphuric acid solution.

5.0 c.c. of isopropyl alcohol ($d_4^{20}$=0.7878; purity 99.0%) and 5.0 c.c. of water were measured in 20–30 c.c. messcylinders with glass stoppers. 5.0 c.c. of various solvents, which were purified by redistillation etc., were added, shaken vigorously and kept on standing at room temperature. The volumes of solvent and water layer were then read at the concave or convex of the meniscus. The results are shown in Table 3.2.

The abilities of the solvents to extract isopropyl alcohol from aqueous layer were roughly compared by the increase of the volume of the solvent layers. The saturated hydrocarbons have little extraction abilities, although unsaturated and aromatic hydrocarbons have larger abilities. Ethers have high ability and especially ethyl ether has the highest ability of extraction. In ethers and aromatic hydrocarbons, the ability of extraction decreases with the larger alkyl radical or with the increase of the number of alkyl radicals. For instance, diisoamyl ether has less ability than ethyl ether, and xylene than benzene. Halogenated hydrocarbons, such as $CCl_4$, $C_2HCl_3$, $C_6H_5Cl$ and $o$-$C_6H_4Cl_2$ have also abilities of extraction. Cyclohexanol, cyclohexanone and furfural mixed homogeneously in the solution.

**3·2. Experimental Results.** The results are shown in Table 3.1. Although various solvents, which seem to be effective, have been found in the preliminary experiments described above, only benzene, *o*-dichlorbenzene and ethyl ether have been tested in the present investigation, and ethyl ether has been found to be the most effective solvent.

In most experiments, about 100–110 g. of isobutylene was absorbed with 143 g. of 67% sulphuric acid (about 1 mol. of $H_2SO_4$) below 20°C. with little polymerisation. . The absorption product, which is composed of the following equilibrium mixture[6], has already the strong smell of

(9) S. Young, Distillation Principles and Processes, (1922), 170.
(10) H. S. Davis and W. J. Murray, *Ind. Eng. Chem.*, **18**(1926), 844.

$$i\text{-}C_4H_8 \underset{-H_2SO_4}{\overset{+H_2SO_4}{\rightleftharpoons}} t\text{-}C_4H_9OSO_3H \underset{-H_2O+H_2SO_4}{\overset{+H_2O-H_2SO_4}{\rightleftharpoons}} t\text{-}C_4H_9OH$$

*tert*-butanol. However, the extraction with benzene (5 times with each 100 c.c. solvent) was not effective (DB 304; 16–30% extracted), the majority of *tert*-butanol remaining unextracted. A small amount of benzene dissolved in the acid layer, and distilled at slightly lower temperature than that of *tert*-butanol water azeotropic mixture, which made the determination of *tert*-butanol obscure. Ethyl ether mixes completely with 67% sulphuric acid and cannot be used without dilution of the acid.

Table 3·2. The Comparison of the Extraction Abilities of various Solvents against aqueous Solution of $i$-$C_3H_7OH$.

| Solvents | B.P. (°C. uncorr.) | Solvent 5.0 c.c. + Water 5.0 c.c. + $i$-$C_3H_7OH$ 5.0 c.c. (30°C.) | | | References |
|---|---|---|---|---|---|
| | | Aqueous layer (c.c.) | Solvent layer (c.c.) | Increase in the solvent layer (c.c.) | |
| Cyclohexane ..... | 80.3- 80.5 | 9.0 | 5.8 | 0.8 | |
| Decaline[1] ..... | 185 -191 | 9.5 | 5.3 | 0.3 | Large menisc |
| Cyclohexene ..... | 82.0- 82.3 | 7.7 | 7.1 | 2.1 | |
| Benzene[2] ..... | m.p. 5.1°C. | 6.6 | 8.2 | 3.2 | |
| Xylene ..... | 135.0-137.5 | 8.3 | 6.6 | 1.6 | |
| $CCl_4$ ..... | 76.3- 76.5 | 6.7 | 8.2 | 3.2 | The solvent layer is lower |
| Trichlorethylene ... | 86.0- 87.0 | 6.5 | 8.4 | 3.4 | ,, |
| $C_6H_5Cl$ ..... | 129.7-130.3 | 6.8 | 8.0 | 3.0 | |
| $o$-$C_6H_4Cl_2$[3] ..... | 175.0-175.5 | 8.5 | 6.3 | 1.3 | |
| Cyclohexanol ..... | 158.0-159.0 | mixes homogenously | | | |
| Cyclohexanone ..... | 153.0-155.0 | mixes homogenously | | | |
| Ethyl ether[4] ..... | — | 4.4 | 10.2 | 5.2 | |
| Diisopropyl ether .. | 67.0- 68.0 | 5.9 | 8.7 | 3.7 | |
| Diisoamyl ether ... | 167.0-169.0 | 8.2 | 6.6 | 1.6 | |
| Anisol ..... | 151.0-153.0 | 7.4 | 7.5 | 2.5 | |
| Nitrobenzene ..... | 205.5-206.5 | 8.8 | 6.1 | 1.1 | Solvent layer is lower |
| Furfural ..... | Redistd. under reduced press. | Mixes homogeneously | | | |

(1) Purified after washing with sulphuric acid.

(2) Commercial pure product was recrystallised 3 times.

(3) Commercial product was redistilled and para-isomer was separated by ice-cooling.

(4) Commercial pure product; other solvents were purified by redistillation.

The dilution of the absorption product with water makes *tert*-butanol readily extractable. In most cases the acid was diluted to the dilution concentration of about $H_2SO_4:H_2O \fallingdotseq 30:70$ or $=29:71$ (by wt.) in detail as described in the experimental details.

By the extraction of the diluted product with benzene (5 times with 100 c.c. benzene; DB 305), 74% of *tert*-butanol was extracted. The dissolution of benzene in the acid phase was negligibly small.

46% of *tert*-butanol was extracted with *o*-dichlorobenzene in the same condition (5 times with 100 c.c. solvent; DB 306). This result is, however, lower than that of benzene, and is parallel with the results of the preliminary experiments. *o*-Dichlorobenzene has a markedly higher boiling point than that of *tert*-butanol.

The extraction with ethyl ether is the most effective, and about 91% of *tert*-butanol was extracted by the 5 times extraction with each 100 c.c. solvent (DB 317), and all *tert*-butanol was extracted by 10 times extraction (DB 307). The increase in the dilution concentration of acid of about 32% (DB 343) decreases the extraction of *tert*-butanol to about 83% by 5 times extraction (cf. DB 317).

In the extraction with ether from diluted acid, the first one portion (in summer) or the first two portions (in winter) of 100 c.c. ether mixes homogenously with acid layer, however, by the addition of the next portion of 100 c.c. solvent, the mixture separates into two layers. A small amount of ethyl ether dissolves in the acid phase, which, however, can be readily fractionated from *tert*-butanol-water azeotropic mixture owing to its large difference in boiling points.

*Some Attempts for the Absorption of Isobutylene with Dilute Sulphuric Acid.* Some attempts were made for the absorption of isobutylene with dilute sulphuric acid and for the extraction of *tert*-butanol without dilution, in order to repeat the absorption with the same acid. Since the rate of absorption of isobutylene with dilute acid was slow[6], $Ag_2SO_4$ was saturated in the acid phase in order to accelerate the absorption[11]. The results are shown in Table 3.1 (DB 359, DB 360, DB 371). The absorption was very slow with 29% sulphuric acid saturated with $Ag_2SO_4$ (DB 359). It is also very slow with 38% sulphuric acid saturated with $Ag_2SO_4$ (DB 360), although slightly more rapid than the case of 29% acid. By repeating the absorption with 38% sulphuric acid, about 81 g. (1.45 mol.) of isobutylene was absorbed approaching to saturation.

## 3·3. Summary.

1. As another method of the separation of *tert*-butanol from the absorption product of isobutylene with sulphuric acid, without neutralisation of the acid with alkali, the extraction of *tert*-butanol with solvents has been investigated. It is necessary to dilute the acid after absorption

(11) cf. W. E. Eberz, H. J. Welge and H. J. Lucas, *J. Am. Chem. Soc.*, **59**(1937), 45; S. Winstein and H. J. Lucas; *ibid.*, **60**(1938), 836; V. N. Morris, *ibid.*, **51**(1929), 1460, etc.

of isobutylene before extraction. Ethyl ether has been found to be the most suitable solvent for the extraction.

2. *tert*-Butanol can be extracted almost completely from the acid phase, different from the case of secondary olefines.

3. The absorption of isobutylene with dilute sulphuric acid, in order to extract *tert*-butanol without dilution, has been found very slow even when the acid phase is saturated with $Ag_2SO_4$.

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*Imperial Fuel Research Institute,*
*Kawaguti, Saitama Prefecture.*