Synthesis of Tertiary Butyl Alcohol by the Hydration of Isobutylene. IV. Some Attempts for the Confirmation of the Formation of Tertiary Butyl Sulphates, and Discussions on the Reaction Mechanism.

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4·1. Some Attempts for the Confirmation of the Formation of *tert*-$C_4H_9OSO_3H$.

Although the formation of *tert*-$C_4H_9OSO_3H$ has been assumed as an intermediate product in the hydration and polymerisation of isobutylene with sulphuric acid⑵, no indication has been observed of its formation in the previous report⑶. In case of the hydration of secondary olefines, such as propylene and *n*-butylene, the formations of *sec*-$ROSO_3H$ and (*sec*-R)$_2SO_4$ were distinctly confirmed⑷, and *sec*-$ROSO_3H$ became very stable by conversion into sodium salt or *sec*-$ROSO_3^-$ ion. In the present investigation some experiments were made for the purpose of the comfirming *tert*-$C_4H_9OSO_3H$ as sodium and barium salts, but no indication of the ester formation was observed.

Since there is the possibility of the decomposition of *tert*-$C_4H_9OSO_3Na$ into *tert*-butanol in the course of the distillation of the alkaline solution, obtained by the neutralization of the absorption product of isobutylene with sulphuric acid, the solution has been extracted at room temperature to remove the free *tert*-butanol completely, and the remaining solution has then been distilled to obtained *tert*-butanol, which is expected to be produced from *tert*-$C_4H_9OSO_3Na$. However, little *tert*-butanol has been obtained by the distillation of the remaining solution, showing that *tert*-butanol corresponding to the amount of isobutylene absorbed had been completely extracted with ether.

The absorption product of isobutylene with 67% sulphric acid was diluted and neutralised by the addition of sodium hydroxide solution with vigorous stirring below 20°C. (DE 309), or it was dropped into excess sodium hydrooxide solution vigorously stirred below 10°C. (DB 308), with the same negative results.

B. T. Brooks and I. Humphrey⑸ reported that they obtained barium salts of acidic sulphates of tertiary alcohols, such as *tert*-$C_6H_{13}OSO_3\frac{Ba}{2}$

⑴ This paper is the 9th report on the hydration of olefines into alcohols; Previous Paper: this Bulletin, **18**(1943), 251.

⑵ cf. M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 392B, 363B, **45**(1942), 211B.

⑶ M. Katuno, *ibid.*, **44**(1941), 392B.

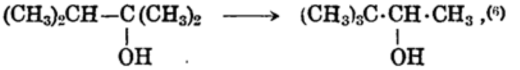
⑷ cf. M. Katuno, *ibid.*, **43**(1940), 8B, 11B, **44**(1941) 275B, 279B.

⑸ B. T. Brooks and I. Humphrey, *J. Am. Chem. Soc.*, **40**(1918), 822.

and *tert*-$C_7H_{15}OSO_3\frac{Ba}{2}$, by treating tetramethyl ethylene and γ-ethyl-β-pentene with sulphuric acid. In the present investigation the separation of barium salt of *tert*-$C_4H_9OSO_3H$ has been attempted, though with negative results.

The absorption product of isobutylene with 67% sulphuric acid below 20°C. was diluted and neutralised by the addition of $Ba(OH)_2\cdot 8H_2O$, or it was dropped into the aqueous suspension of excess $Ba(OH)_2\cdot 8H_2O$, vigorously stirred. After removing an excess of barium hydroxide by filtration and by precipitation with saturation of carbon dioxide followed by filtration of barium carbonate, the filtrate was evaporated in a bath under reduced pressure at 45°C. A small amount of barium salt corresponding to the formula $C_4H_9OSO_3\frac{Ba}{2}$ was obtained. It was very stable and the decomposition of its acidic solution yielded not *tert*-butanol, but *sec*-butanol, showing that the salt obtained was *sec*-$C_4H_9OSO_3\frac{Ba}{2}$ which, probably, had been produced from normal butylene contained as impurity in isobutylene gas. Thus *tert*-$C_4H_9OSO_3H$ has not been confirmed in the present investigation.

It is also doubtful that the barium salts obtained by Brooks and Humphrey contain tertiary radicals, because there is the possibility of the rearrangement of tertiary alkyl radical into secondary, such as



$$(CH_3)_2CH-\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2 \longrightarrow (CH_3)_3C\cdot\underset{\displaystyle OH}{\underset{|}{CH}}\cdot CH_3\ ,^{(6)}$$

and of the existence of secondary isomeric olefines contained as impurities.

Experimental Details. 1. *Experiment for the Confirmation of* *tert*-$C_4H_9OSO_3Na$, *No. 1.* (DB 309). 76.5 g. (1.365 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid with vigorous stirring at 15–17°C. for $4\frac{15}{60}$ hrs. The product was diluted with 190 g. of water with vigorous stirring below 20°C., and then made strongly alkaline to phenolphthalein with concentrated sodium hydroxide solution below 20°C.

tert-Butanol separated was removed and the aqueous layer was extracted five times with each 100 c.c. of ether, after dissolving sodium sulphate by adding water and warming slightly. The aqueous solution obtained was distilled through a 30 cm. Widmer column to obtain a distillation curve against the weight of the distillate. The boiling point rised rapidly to that of water, after a small amount of ether dissolved, had been distilled away, but little *tert*-butanol-water azeotropic mixture (b.p. 79.9°C) was observed.

2. *Experiment for the Confirmation of* *tert*-$C_4H_9OSO_3Na$, *No. 2.* (DB 308).. 72.5 g. (1.295 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid with vigorous stirring for $6\frac{20}{60}$ hrs. at 15–18°C. The product was dropped into 20% sodium hydroxide solution (450 g.)

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(6) K. C. Laughlin, C. W. Nash and F. C. Whitmore, *J. Am. Chem. Soc.*, **56** (1934), 1395; F. C. Whitmore and P. L. Meunier, *ibid.*, **63** (1941), 2197.

which was stirred vigorously and cooled below 10°C. Water was added, if necessary, in the course of the neutralisation. The product was diluted with water to about 1 l. and slightly warmed to dissolve sodium sulphate completely. Then it was extracted five times with each 100 c.c. ether. The aqueous solution, separated from free *tert*-butanol was refluxed for 2 hrs, and then distilled, using a 30 cm. Widmer column, to draw a distillation curve. The boiling point rised rapidly to that of water after distilling a small amount of ether, but *tert*-butanol-water azeotropic mixture was hardly observed.

3. *The Experiment to separate tert*-$C_4H_9\cdot OSO_3\frac{Ba}{2}$, *No. 1.* (DB 301). 51.2 g. (0.915 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid for $4\frac{40}{60}$ hrs. with vigorous stirring at 18–21°C. The product was diluted with 200 c.c. of water below 20°C. with stirring and 400 g. (1.27 mol.) of the powder of $Ba(OH)_2\cdot 8H_2O$ was added little by little with vigorous stirring below 20°C., water being added when necessary. The product was filtered from barium sulphate and excess $Ba(OH)_2\cdot 8H_2O$, and saturated with CO_2, then filtered from barium carbonate. The filtrate was evaporated in a thermostat under reduced pressure at 45°C. and about 3.4 g. of white solid was obtained.

4. *The Experiment for the Separation of* tert-$C_4H_9OSO_3\frac{Ba}{2}$, *No. 2.* (DB 303). 53 g. (0.95 mol.) of isobutylene was absorbed with 143 g. of 67% sulphuric acid for $6\frac{15}{60}$ hrs. at 14–18°C. The product was dropped into the mixture of 300 c.c. water and 377 g. (1.2 mol.) of the powder of $Ba(OH)_2\cdot 8H_2O$, stirred vigorously and cooled below 10°C. The product showed alkaline to phenolphthalein.

The product was filtered, and the filtrate was saturated with carbon dioxide to precipitate barium carbonate, which was then filtered. The filtrate was evaporated in the thermostat under reduced pressure at 45°C, and 4.6 g. of white crystalline solid was obtained.

The white solid obtained in both of the experiments is soluble in water, and precipitates barium sulphate by the addition of sulphuric acid. On boiling its aqueous solution, however, it is stable and does not precipitate barium sulphate by the decomposition.

Anal. C: 20.21%, 20.20%; H: 4.33%, 4.32%; Ba: 28.24%, 28.39%.

Calcd. for $C_4H_9OSO_3\frac{Ba}{2}$: C: 21.65%; H: 4.09%; Ba 30.96%.

5. *The Isolation of sec*-C_4H_9OH *from the* $C_4H_9OSO_3\frac{Ba}{2}$. 2.7 g. of the $C_4H_9OSO_3\frac{Ba}{2}$ obtained was dissolved in 3.5 c.c. of water, and was then mixed with 42 g. of 60% sulphuric acid, when barium sulphate precipitated. After being kept on standing 3 hrs., 33 c.c. of water was added below 20°C. and then made strongly alkaline with 120 g. of 20% sodium hydroxide solution. Phenolphthalein was not added to avoid the contaminating by ethyl alcohol. The product was then distilled with a 20 cm. Widmer column and 8.8 g. of distillate boiling at 97–99°C was obtained (Distillate A). The residue was then distilled after acidifying with 100 g.

of 50% sulphuric acid(7), and 10.5 g. of distillate boiling at 98–99°C. was obtained (Distillate B). The reactions of both distillates and those of *sec*- and *tert*- butanol are as follows.

	Distillate A	Distillate B	*sec*-C_4H_9OH	*tert*-C_4H_9OH
Iodoform reaction	Faint	Positive	Positive	Negative
Reaction against conc. HCl	Transparent	Transparent	Transparent	Turbulent
Reaction against Nessler reagent ...	Weak	Orange ppt.	Orange ppt.	Faint ppt.

Thus the distillates showed not the reactions of *tert*-butanol, but those of *sec*-butanol. The concentration of *sec*-butanol is small in the distillate A. The barium salt obtained is, therefore, *sec*-$C_4H_9OSO_3\frac{Ba}{2}$, derived from normal butylenes probably contained as impurities in the isobutylene gas.

4·2. Discussion on the Reaction Mechanism of Hydration of Isobutylene.

The hydration of isobutylene, which belongs to the tertiary olefine, is markedly different from that of secondary olefines, such as, propylene and *n*-butylenes. Namely, (1) isobutylene can be absorbed rapidly with more dilute sulphuric acid, and it is polymerised more readily than secondary olefines, as is well known. (2) *tert*-Butanol formed in the acid phase can be extracted completely from the absorption product of isobutylene with sulphuric acid after being diluted with water, while in case of secondary olefines(8) a considerable amount of secondary alcohol remains unextracted in the form of stable acidic sulphate. (3) *tert*-Butanol can be completely recovered by distillation or by extraction from the absorption product of isobutylene with sulphuric acid, after being neutralized with excess alkali, in contrast with the fact that, in case of secondary olefine, a considerable amount of alcohol exists in the form of the stable acidic sulphate salt, such as *sec*-$C_4H_9OSO_3Na$(9), which undergoes little hydrolysis. (4) No formation of di-*tert*-alkyl sulphate was observed even when isobutylene was absorbed with 67% sulphuric acid to saturation, while in case of secondary olefines, such as propylene and *n*-butylene, di-*sec*-alkyl sulphate was formed and easily separated(10)

The above differences can be readily explained by the analogous reaction mechanism as in the hydration of secondary olefines(11), only by assuming the rapid hydrolysis of sulphuric acid ester of *tert*-butanol, forming the following equilibrium state.

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(7) M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 275B, Expt. DA25.

(8) B. T. Brooks, *Ind. Eng. Chem.*, **27**(1935) 282.

(9) M. Katuno, *J. Soc. Chem. Ind., Japan*, **44**(1941), 275B.

(10) B. T. Brooks, *Ind. Eng. Chem.*, **27**(1935), 282; M. Katuno, *J. Soc. Chem. Ind., Japan*, **43**(1940), 11B; **44**(1941), 275B.

(11) M. Katuno, *ibid.*, **43**(1940), 8B, 11B; **44**(1941), 275B.

$$i\text{-}C_4H_8 \underset{-H_2SO_4}{\overset{+H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9\cdot OSO_3H \underset{-H_2O+H_2SO_4}{\overset{+H_2O-H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9OH$$

There seems no necessity to assume other reaction mechanism, which differs essentially from that for the hydration of secondary olefines, for the hydration of tertiary olefine. Sulphuric acid is added to the double bond of isobutylene reversibly to form *tert*-$C_4H_9OSO_3H$, which is highly reactive and undergoes hydrolysis immediately to establish the above equilibrium. *tert*-$C_4H_9OSO_3H$ is an important intermediate compound not only in the hydration of isobutylene, but also in the polymerisation of isobutylene according to the most reliable mechanism of the type of Lwow(12).

The assumption of the high reactivity for *tert*-$C_4H_9OSO_3H$ is probable, judging from the following facts concerning the high reactivity of tertiary alkyl radicals. Namely, *tert*-butanol is converted immediately into *tert*-butyl chloride,(13) by mixing with concentrated hydrochloric acid, while the analogous reactions of primary and secondary alcohols are slow. Tertiary alkyl chlorides, in general, undergo more rapid hydrolysis than secondary and primary alkyl chlorides(14). *Tert*-butyl acetate is more readily hydrolised than *sec*- and *prim*-alkyl acetates in neutral or acidic solution(15) although less readily in alkaline(16). It reacts rapidly with hydrobromic acid(15a). Ethers containing *tert*-alkyl radicals, including the recently known di-*tert*-butyl ether(17), undergo decomposition readily with acids.(18)

The fact that no indication of the formation of *tert*-butyl sulphate could be found in the present investigation may also be explained as follows. Namely, although *tert*-$C_4H_9OSO_3H$ may be formed in the equilibrium mixture, it is hydrolysed completely into *tert*-butanol, on the dilution and neutralisation with alkali, due to the rapid shift of the equilibrium. The fact that the same results are obtained even when the absorption product is dropped into the alkaline solution vigorously stirred, suggests that the hydrolysis of *tert*-$C_4H_9OSO_3H$ takes place very rapidly. The complete extraction of *tert*-butanol from the sulphuric acid solution can also be readily explained by the above equilibrium. It is not yet known whether *tert*-$C_4H_9OSO_3Na$ is stable like *sec*-$ROSO_3Na$ or not.

Although the formation of di-*tert*-butyl sulphate ((*tert*-$C_4H_9)_2SO_4$)

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(12) M. Katuno, *ibid.*, **44** (1941), 363B; cf. Kondakow, J. Prakt. Chem., (2) **54** (1896), 442.

(13) "Organic Synthesis."

(14) E. E. Ayres, *Ind. Eng. Chem.*, **21** (1929), 899; H. M. Woodburn and F. C. Whitmore, *J. Am. Chem. Soc.*, **56** (1934), 1394.

(15) H. S. Davis and W. J. Murray, *Ind. Eng. Chem.*, **18** (1926), 844; A. Skrabal and A. M. Hugetz, Monatsh, **47** (1928), 17; M. H. Palomaa, *etal.*, *Ber.*, **68** (1935), 303; (15a) B. W. Tronow and N. C. Ssibgatulin, *Ber.*, **62** (1929), 2850.

(16) A. Skrabal and A. M. Hugetz, loc. cit.; W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **58** (1936), 1014.

(17) J. L. E. Erickson and W. H. Ashton, *ibid.*, **63** (1941), 1769.

(18) J. F. Norris and G. Y. Rygby, *ibid.*, **54** (1932), 2088; T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28** (1936), 1186.

was not observed, there would be the possibility of its formation according to the following equilibrium,

$$t\text{-}C_4H_9\cdot OSO_3H + t\text{-}C_4H_9OH \rightleftarrows (t\text{-}C_4H_9)_2SO_4 + H_2O$$

or

$$2\,t\text{-}C_4H_9\cdot OSO_3H \rightleftarrows (t\text{-}C_4H_9)_2SO_4 + H_2SO_4$$

and it may disappear immediately due to the shift of equilibrium, on dilution or neutralisation.

Isobutylene can be slowly absorbed with dilute acid of less than 1 N concentration(19). H. J. Lucas and W. F. Eberz(19) used the following hydration mechanism including hydrogen ion.

$$i\text{-}C_4H_8 + H_3O^+ \longrightarrow t\text{-}C_4H_9OH + H^+$$

However, the rapid absorption of isobutylene with concentrated acid, such as 67% in weight shows that the reaction with undissociated sulphuric acid, as shown by the mechanism described above, takes place rapidly.

4·3. Summary.

1. The confirmation of *tert*-$C_4H_9OSO_3H$, which has been assumed as the intermediate compound in the hydration and polymerisation of isobutylene with sulphuric acid, has been attempted in the form of sodium or barium salts though with negative results.

2. The reaction mechanism of the hydration reaction of isobutylene with sulphuric acid has been discussed. Experimental results can be explained by the assumption that *tert*-$C_4H_9OSO_3H$ formed is very reactive to undergo rapid hydrolysis to establish the following equilibrium rapidly.

$$i\text{-}C_4H_8 \underset{-H_2SO_4}{\overset{+H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9\cdot OSO_3H \underset{-H_2O+H_2SO_4}{\overset{+H_2O-H_2SO_4}{\rightleftarrows}} t\text{-}C_4H_9OH$$

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(19) H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56** (1934), 460; H. J. Lucas and Y. P. Lin, *ibid.*, **56** (1934), 2138.