

HYDROLYSIS OF TERTIARY ALKYL HALIDES

NICHOLAS D. CHERONIS

Wright Junior College, Chicago, Illinois

The hydrolysis of tertiary halides has been reported several times in the literature.^{1,2,3} There is quite a disagreement, however, as to relative amounts of carbinol and olefin in the results reported. French, McShan and Johler report on the hydrolysis of tertiary butyl chloride at 50° C. using 0.01 normal alkali (KOH) a yield of 96.71 per cent of carbinol and 1.3 per cent of olefin. On the other hand, Woodburn and Whitmore report the hydrolysis of tertiary amyl chloride and bromide, both at room and reflux temperatures, and in presence and absence of alkali, yield mostly olefin at higher temperatures.

The methods of analysis used by French and his collaborators are to collect olefin over water and then to estimate it by gasometric analysis. The carbinol was determined by the refractive indices of the aqueous distillates. Woodburn and Whitmore fractionate the aqueous and organic layers through an adiabatic column. The data as to the composition of the hydrolytic mixture do not seem to be quantitative.

In an extensive investigation of the rates of ammonolysis of the alkyl halides,

it was noted that the tertiary alkyl halides react very rapidly with both aqueous and alcoholic ammonia to yield large amounts of olefins and very little amine. This observation and the lack of agreement in the literature as to the composition of the hydrolytic mixtures of alkyl halides led to the present investigation.

Method.—Measured amounts of the halides and water were sealed in ampoules and heated at the temperature indicated. The ampoules were rapidly cooled, opened, and the contents extracted with purified n-hexane. The organic layer was analyzed for unreacted halide by shaking with standard silver nitrate and for olefin by using standard bromide-bromate. The accuracy of this method for the estimation of olefin in presence of halide and carbinol was carefully checked, using known amounts of 2-methyl-butene-2. For samples containing as little as 30 mgs. of olefin, the error was not above 20 parts per thousand.

Results.—The results of several runs are summarized in tables I, II, and III.

Table I shows the composition of the equilibrium mixture when one mole of

TABLE I—HYDROLYSIS OF TERTIARY AMYL HALIDES AT 100° C.
(one mole halide : 10 moles water)

Halide	No.	Time heated hrs.	Halide ion produced %	Unreacted halide %	Total %	Olefin %	Carbinol %
Chloride.....	120	100					
Chloride.....	121	100	70.9	27.5	98.4	60.2	12.3
Bromide.....	102	100	70.7	29.2	99.9	60.1	10.7
Bromide.....	103	100	87.8	10.2	98.0	61.4	28.4
Iodide.....	122	100	88.5	8.8	97.3	60.7	30.5
Iodide.....	123	100	87.6	10.7	98.3	49.5	39.8
Bromide ^a	124	100	87.3	10.2	97.5	51.0	38.8
Bromide ^b	125	100	99.3	0.2	99.5	83.5	16.1
Bromide ^b			99.1	0.4	99.5	81.1	18.5

^a One mole of sodium hydroxide added.

^b Sodium hydroxide, 2.5 moles added.

tertiary amyl halide is hydrolyzed with ten moles of water at 100° C. The extent of hydrolysis is the same in the case of bromide and iodide but less for the chloride, while the amount of olefin is about 60 per cent for the chloride and bromide, and 50 per cent for the iodide. Alkali increases the amount of olefin but does not suppress entirely the formation of carbinol.

The conclusion that equilibrium mixtures result is shown in table II. Approximately the same composition is obtained in samples of: (a) One mole of bromide with 10 moles of water; (b) One mole of carbinol with one mole of hydrogen bromide and nine moles of water;

(c) One mole of olefin with one mole of hydrogen bromide and 10 moles of water.

The effect of increase in the amount of water is shown in table III. As expected, the amount of amyl bromide decreases, but olefin, rather than carbinol shows an increase.

Comparison with the results obtained with tertiary butyl bromide shows some unexpected results. The amount of olefin is negligible, diminishing rather than increasing with alkali.

The conclusion is reached that no single generalization can be made about the hydrolysis of tertiary alkyl halides. The influence of the radical on the direction of the reaction is very marked.

TABLE II—COMPOSITION OF EQUILIBRIUM MIXTURES OBTAINED BY:

- a. Hydrolysis of tert-amyl bromide
b. Hydrogen bromide and tert-amyl alcohol
c. Hydrogen bromide and 2-methyl-butene-2 at 100° C.

Mixture	No.	Hours heated	Halide Ion produced %	Unreacted halide %	Olefin %	Carbinol %
Bromide-1 mole, Water-10 moles-----	100	100	88.4	7.1	60.7	32.1
	101	100	89.2	7.1	60.1	32.9
ter-amyl alcohol-1 mole, Water-9 moles, HBr-1 mole-----	108	100	88.7	8.1	61.4	30.3
	109	100	91.1	7.2	60.1	32.4
2-methyl-butene-2—1 mole, Water-9 moles, HBr-1 mole-----	110	100	90.5	9.05	60.6	30.3
	111	100	93.0	8.1	60.1	31.1

TABLE III—COMPOSITION OF HYDROLYSIS MIXTURES OF TERTIARY BUTYL AND AMYL BROMIDES UNDER VARIOUS CONDITIONS

Tertiary Bromide	Moles of H ₂ O per one mole Halide	Temp. °C.	Time heated hrs.	Composition			Carbinol %
				Halide Ion %	Unreacted Halide %	Olefin %	
Amyl-----	10	100	24	89.2	7.1	60.7	32.1
	40	100	24	98.6	1.7	70.8	27.5
Amyl-----	100	100	24	98.0	0.9	77.1	22.0
Amyl-----	100	100	24	99.5	0.0	9.5	90.5
Butyl-----	100	50	24	99.2	0.0	1.3	98.7
Butyl-----	100	100	24	89.9	9.2	40.9	49.1
Butyl-----	10	100	24	99.6	0.0	3.2	96.8
Butyl-----	100 ^a	50	24	99.2	0.0	5.4	94.6
Butyl-----	100 ^b	100	24				

^a Plus 3.75 moles of NaOH.

^b Plus 3.75 moles of NaOH.

¹ H. E. French, W. H. McShan and W. W. Jöhler, JACS 56, 1347.

² H. Milton Woodburn and F. C. Whitmore, JACS 56, 1394.

³ Edward Hughes, JACS 57, 708.