The Ammonolysis of Butyl Halides

Nicholas D. Cheronis

Chicago City Colleges, Chicago, Illinois

The study of the ammonolysis of the butyl halides is part of a general investigation on the ammonolysis of halogen compounds.

The reaction of an alkyl halide with aqueous ammonia involves formation of amines, alcohols, olefins and ethers, depending on the nature of halide and conditions under which the reaction takes place.

The rate of reaction is determined fairly accurately by analysis for a halide ion by standard methods. A modification must be made in the case of ter-butyl halides as they react rather rapidly with silver nitrate. The sample in such cases is rapidly evaporated under reduced pressure until ammonia, solvent and unreacted halide have been removed.

A new method was developed for the estimation of primary amines. Briefly, as applied to the butyl amines, it is as follows: The sample, made strongly alkaline, is extracted with ether. The extract is shaken for one minute with specially prepared silver chloride and then for one minute with sodium cobaltinitrite. The ether extract is filtered, titrated with 1.0 N HCl and the ether evaporated. The residue is made to standard volume. The primary amine is determined by the micro-Van Slyke method, while the secondary and tertiary are determined by a modification of Weber and Wilson's method.*

Table 1 shows the rates of ammonolysis of the four butyl bromides in alcoholic-aqueous ammonia at 25°C. Table II shows the composition of the final equilibrium mixture. Table III, the effect of various concentrations of ammonia on the amounts of various amines formed, and Table IV, the rate of ammonolysis of n-butyl bromide in aqueous ammonia at 60 and 100°C.

These results seem to indicate that higher conversion to amines takes place in the straight chain halides; the tertiary reacts rapidly, but less than ten per cent is converted to amine with olefin formation assuming a dominant role. Increase in the ratio of ammonia to the halide increases the amount of primary amine. Using four moles of ammonia to one of n-bromide, the formation of primary amine is rapid up to the half point of the reaction, then drops as the secondary and tertiary amines are formed at a more rapid rate than before. The relative amounts of the three amines are not greatly affected by increase in temperature.

Ammonolysis in aqueous system takes place at the interface of the halide and aqueous layers; it is slow at 60°C. but fairly rapid at 100°C. The composition of the final equilibrium mixture is not appreciably different for aqueous or alcoholic (90 per cent alcohol) ammonia systems. Catalysts such as copper and other metals do not have any effect at temperatures of 100°C., while substances which increase the surface by dispersion of the immiscible halide accelerate the reaction.

SUMMARY

1. The rate of ammonolysis of the four butyl bromides was measured at 25° and 60°C. with alcoholic ammonia.
2. The ammonolysis of n-butyl chloride with aqueous ammonia was measured at 60° and 100°C.
3. The influence of temperature and ammonia concentration on the equilibrium mixtures was determined.

* Journ. of Am. Biol. Chem., 35:385 (1918).

TABLE I—RATES OF AMMONOLYSIS OF BUTYL BROMIDES WITH ALCOHOLIC AMMONIA* AT 25° C.

Bromide	Time required for conversion of 0.5 mole of bromide	Reactivity	Total conversion to amines	Per cent conversion to amines
	Hours		Moles	
ter-Butyl	2.0	1,000	0.07	14.0%
n-Butyl	14.5	138	0.50	100.0%
sec-Butyl	266.0	7.5	0.48	96.0%
iso-Butyl	480.0	4.1	0.40	80.0%

* 20% ammonia in 90% methanol.

TABLE II—AMMONOLYSIS OF BUTYL BROMIDES WITH ALCOHOLIC AMMONIA* AT 25° C.

COMPOSITION OF THE FINAL EQUILIBRIUM MIXTURE

Bromide	Time	Halide ion produced	Total conversion to amines	Per cent conversion to amines	$R\text{-}NH_2$ %	R_2NH %	R_3N %
	Hours	Moles	Moles				
Tertiary	12	1.00	0.085	8.5%	5.8	------------	------------
Normal	131	0.978	0.94	97.0%	32.4	41.6	20.3
Secondary	885	0.94	0.93	99.0%	76.0	9.0	8.4
iso-	885	0.875	0.716	81.9%	44.4	17.5	19.7

* 20% ammonia in 90% methanol.

TABLE III—AMMONOLYSIS OF N-BUTYL BROMIDE AT 25° C.

(Effect of Ammonia Concentration)

Ratio of $BuBr:NH_3$	Time	Temp. °C.	Halide ion production	Total conversion to amines	Per cent conversion to amines	RNH_2 %	R_2NH %	R_3N %
	Hours		Moles	Moles				
1:4	313	25	0.978	0.94	97.0	32.4	41.6	20.3
1:8	100	25	0.970	0.97	100.0	53.0	12.4	31.6
1:60	80	25	1.00	0.997	99.7	82.5	11.4	5.8
1:4	6	60	0.995	0.995	100.0	43.0	44.2	12.3

Table IV—Ammonolysis of n-Butyl Chloride with Aqueous Ammonia at 60° and 100° C.

(Ratio of Halide to Ammonia 1:4)

Run number	Moles of halide	Diameter of ampule	Temp. °C.	Time hours	Halide ion produced	Amine produced total %	RNH_2 %	R_2NH %	R_3N %
655	0.01	16	60	60	31.4	----------	--------	--------	--------
656	0.02	16	60	83	16.4	----------	--------	--------	--------
657	0.01	21	60	83	38.1	----------	--------	--------	--------
661*	0.01	16	60	83	49.1	----------	--------	--------	--------
783†	0.01	16	60	83	72.4	----------	--------	--------	--------
630	0.02	21	60	151	50.1	47.6	25.1	12.0	10.5
631	0.02	21	60	384	88.7	84.0	38.8	20.6	24.6
632	0.02	21	100	48	99.5	84.2	39.2	23.4	21.6
660‡	0.02	21	100	6	.993	89.6	38.4	29.6	21.5

* Clay, 83 mg. added.
† Bentonite, 83 mg. added.
‡ With 4 moles alcoholic ammonia.